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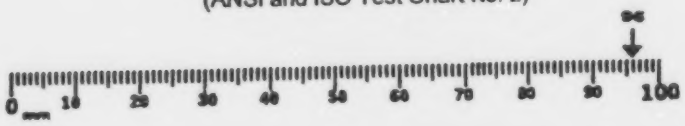

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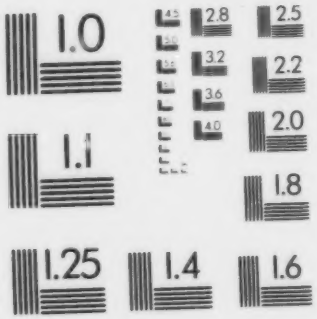

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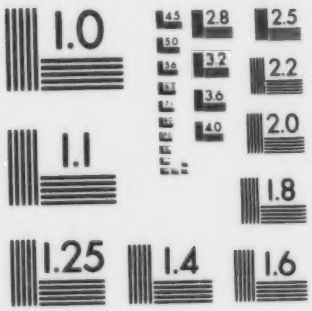

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A Comprehensive Multiresidue Ultra-Trace Analytical Method, Based on HRGC/HRMS, for the Determination of PCDDs, PCDFs, PCBs, PBDEs, PCDEs, and Organochlorine Pesticides in Six Different Environmental Matrices

M.G. Ikonomou, T. Fraser, N.F. Crewe, M.B. Fischer, I.H. Rogers, T. He, P.J. Sather, and R.F. Lamb

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Sidney, British Columbia V8L 4B2

2001

Canadian Technical Report of Fisheries and Aquatic Sciences 2389

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A COMPREHENSIVE MULTIRESIDUE ULTRA-TRACE ANALYTICAL METHOD, BASED ON HRGC/HRMS, FOR THE DETERMINATION OF PCDDS, PCDFS, PCBS, PBDES, PCDES, AND ORGANOCHLORINE PESTICIDES IN SIX DIFFERENT ENVIRONMENTAL MATRICES

by

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I.H. Rogers, T. He, P.J. Sather, and R.F. Lamb

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ABSTRACT

Ikonomou, M.G., T.L. Fraser, N.F. Crewe, M.B. Fischer, I.H. Rogers, T. He, P.J. Sather, and R.F. Lamb. 2001. A comprehensive multiresidue ultra-trace analytical method, based on HRGC/HRMS, for the determination of PCDDs, PCDFs, PCBs, PBDEs, PCDEs, and organochlorine pesticides in six different environmental matrices. Can. Tech. Rep. Fish. Aquat. Sci. 2389: vii + 95 p.

This manual is a description of the methods used in the Regional Dioxin Laboratory (RDL) at the Institute of Ocean Sciences, Sidney, British Columbia for the preparation and analysis of samples for the ultratrace analysis of: polychlorinated dibenzo-*p*-dioxins (PCDDs); polychlorinated dibenzofurans (PCDFs); polychlorinated biphenyls (PCBs); polychlorinated diphenyl ethers (PCDEs); polybrominated diphenyl ethers (PBDEs) and pesticides. The RDL analyses these contaminants in: biological tissue, marine sediment, municipal waste incinerator sampling trains, plasma, serum, and milk. Analysis of each of these classes of compounds are conducted using high-resolution gas chromatography / high-resolution mass spectrometry (HRGC/HRMS).

RÉSUMÉ

Ikonomou, M.G., T.L. Fraser, N.F. Crewe, M.B. Fischer, I.H. Rogers, T. He, P.J. Sather, and R.F. Lamb. 2001. A comprehensive multiresidue ultra-trace analytical method, based on HRGC/HRMS, for the determination of PCDDs, PCDFs, PCBs, PBDEs, PCDEs, and organochlorine pesticides in six different environmental matrices. Can. Tech. Rep. Fish. Aquat. Sci. 2389: vii + 95 p.

Ce document décrit les méthodes utilisées au Laboratoire Régional de Dioxines (LRD) de l'Institut des Sciences Océaniques de Sidney, Colombie-Britanique lors de la préparation et l'analyse ultra-trace des composés dibenzo-*p*-dioxines polychlorées (DDPC), dibenzofuranes polychlorées (DFPC), biphényles polychlorés (BPC), diphényléthers polychlorés (DEPC), diphényléthers polybromés (DEPB) et de pesticides organochlorés. Le LRD effectue l'analyse de ces contaminants dans diverses matrices incluant les tissus biologiques, les sédiments marins, les collecteurs d'émissions atmosphériques provenant d'incinérateur de déchets municipaux, le plasma, le sérum et le lait. Toutes les analyses sont réalisées par chromatographie gazeuse couplée à la spectrométrie de masse à haute résolution (CG/SMHR).

INTRODUCTION

This manual is a description of the methods used in the Regional Dioxin Laboratory (RDL) at the Institute of Ocean Sciences, Sidney, British Columbia. These methods are used to prepare samples for the ultratrace analysis of: polychlorinated dibenzo-*p*-dioxins (PCDDs); polychlorinated dibenzofurans (PCDFs); polychlorinated biphenyls (PCBs); polychlorinated diphenyl ethers (PCDEs); polybrominated diphenyl ethers (PBDEs) and pesticides. The RDL analyses these contaminants in: biological tissue, marine sediment, municipal waste incinerator sampling trains, plasma, serum, and milk. Analysis of each of these classes of compounds are conducted using high-resolution gas chromatography / high-resolution mass spectrometry (HRGC/HRMS).

These methods have evolved since the RDL was staffed in 1991. They are based upon Environment Canada's method for the determination of PCDDs and PCDFs in pulp mill effluents (Anon. 1992) and U.S. Environmental Protection Service Method 1613 (Anon. 1994). An earlier version of these methods has been published (Rantalainen et al. 1998) for the preparation and analysis of PCDD/Fs and PCBs in tissue and lipid.

The general developmental approach in the RDL is to have one sample extracted to yield as many quantifiable contaminants as possible. Our current sample preparation scheme for PCDD/Fs, PCBs, PCDEs, and PBDEs means that one sample may be analysed for all of these compounds with a single extraction. Additional standard spiking plus a sample split following initial extraction can be used to add more acid-sensitive compounds such as pesticides to the list of compounds quantifiable from a single sample. This is an especially powerful approach for unique, biological samples. Analysing these samples using the resolving abilities of HRGC and the specificity of HRMS results in high quality contaminant data with detection limits as low as 50 ppq. The flowchart following this section illustrates the procedure for preparing and analysing a typical tissue sample for PCDD/Fs, PBDEs, PCBs, and pesticides.

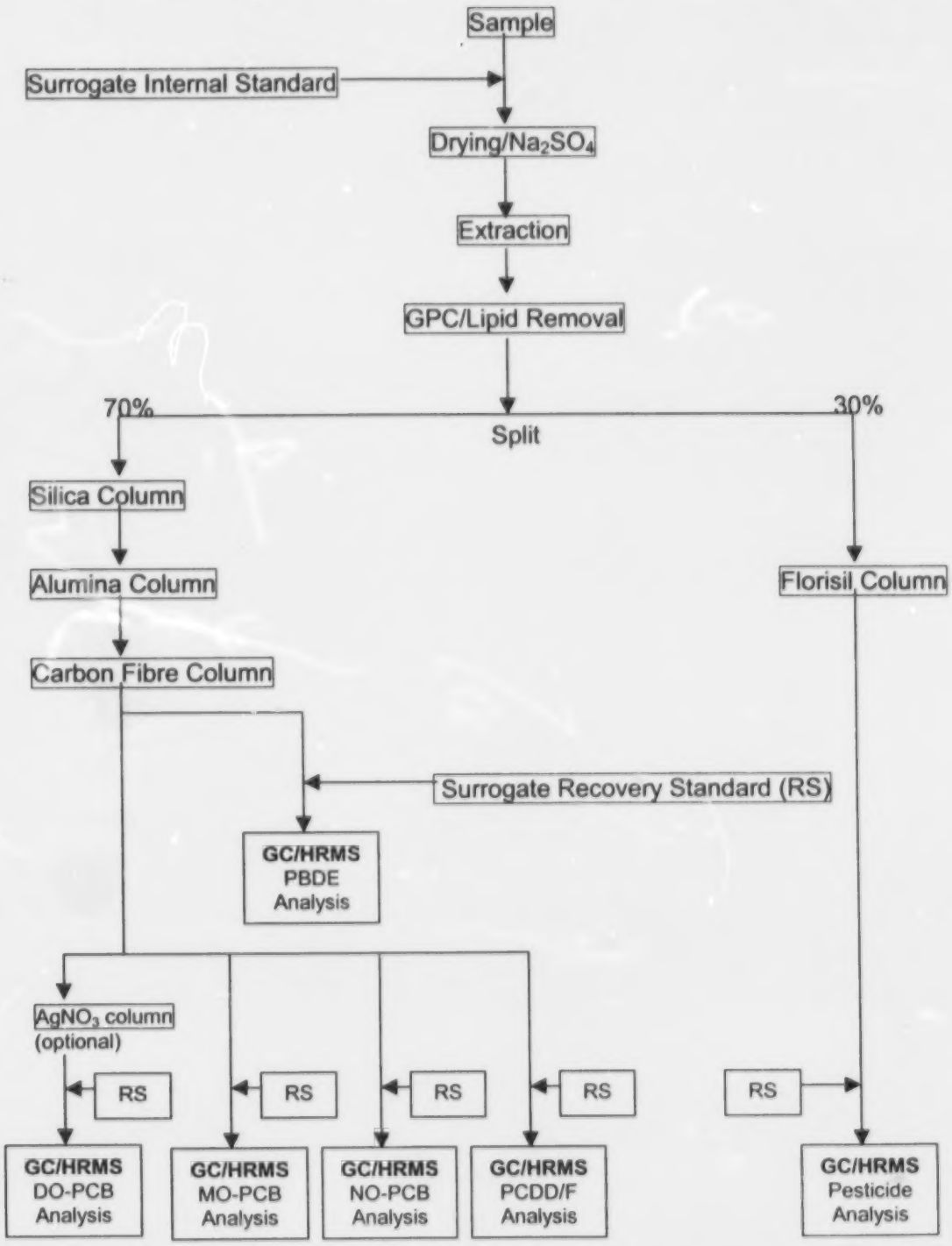
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) is considered to be one of the most toxic compounds known. All of the remaining 2,3,7,8-substituted PCDD/Fs and some PCBs have toxicity values assigned relative to 2,3,7,8-TCDD (Van den Berg et al. 1998). Environmental samples occasionally contain nanogram (10^{-9} g) amounts of PCBs and PCDD/Fs, which are known to have toxic effects in quantities one thousand times less. Worker safety is an extremely important issue in any chemistry laboratory but is even more important in a laboratory handling large volumes of chlorinated and aromatic organic solvents, potentially toxic quantities of PCBs and PCDD/Fs, and working with the reality of a production-oriented schedule. Laboratory safety equipment such as

high face-velocity fumehoods, highly trained laboratory analysts, and careful laboratory safety procedures integrate to make a safe, low-exposure, and highly productive laboratory working environment.

This manual is organised in three main parts:

1. Sample extraction and clean up methods
2. Instrumental method of analysis
3. Appendices of instrumental and quality assurance information.

MULTIRESIDUE ANALYSIS



GENERAL SAMPLE PREPARATION: ALL SAMPLE TYPES

Samples are passed from the archive to the sample preparation laboratory with a sample submission sheet. Both the person who submits the sample from the archive and the laboratory analyst sign the sheet to document changes in sample custody. All batches are ranked such that the samples are processed beginning with the least-contaminated sample (the procedural blank) and ending with the most contaminated sample. This is also the order in which the samples are analysed. This ranking of the samples is an attempt to minimise the instances of high sample to low sample cross-contamination in both extraction and analytical processes.

Information specific to the batch in terms of special preparation steps, shortcuts and sample splits are identified on the sample submission sheet. It also describes the exact standard spiking requirements of the samples, the analytes for which the sample is to be analysed, fractions to be retained but not analysed, who will be doing the lipid and or moisture analyses, and the client code. Copies of the sheet are kept in binders at the quality assurance step and at the mass spectrometer's data station to pass along spiking information, sample weights, lipid and moisture data, record data file names, and vial storage location.

Each batch consists of 12 samples:

- 1 procedural blank
- 9 samples
- 1 replicate sample
- 1 certified reference material (CRM)

For tissue batches the RDL uses one of three CRMs (Cambridge Isotope Laboratories (CIL), Andover, MA):

Tissue type	Matrix type	CIL Product Number
Herring	Clean	EDF-2524
Trout	Contaminated	EDF-2525
Salmon	Fortified	EDF-2526

MOISTURE DETERMINATION

For each sample or replicate:

1. The weight of the aluminum weighing boats for each determination, 2 per sample, is measured and recorded.
2. 3 g of sample is weighed accurately into a pre-weighed weighing boat. Each sample's moisture determination should be done in duplicate.
3. The sample is dried in a 40 °C vented oven for at least 48 hours. It is then cooled completely in a desiccator and the weight recorded (yields dry sample weight).
4. The sample and weighing boat are discarded.
5. Percent moisture is calculated using the following equation:

$$\frac{\text{(Wet sample weight)-(dry sample weight)}}{\text{wet sample weight}} \times 100\%$$

LIPID DETERMINATION

Many lipid determination methods use chloroform:methanol mixtures to extract all lipidaceous material. Our laboratory uses 1:1 DCM:hexane to extract samples for lipid determination. We also filter samples that appear cloudy before lipid weight determination to remove more insoluble materials such as phospholipid and sterols. We believe that this method of determining lipid weight more accurately reflects the amount and nature of lipid extracted by our sample preparation procedures.

Materials

- sodium sulfate: anhydrous, granular sodium sulfate (Mallinckrodt Baker, Inc., Paris, Kentucky) baked at 450 °C at least overnight and cooled to room temperature in a desiccating chamber.
- 1:1 DCM:hexane (both solvents pesticide residue analysis grade, Caledon Laboratories Ltd., Georgetown, Ontario).
- Glass wool
- porcelain mortar: 400 mL capacity (Coors, Golden, CO).
- porcelain pestle: 194 mm long (Coors, Golden, CO).

Equipment

- Extraction columns used for lipid determination: total length of column approximately 40 cm (2.5 cm long X 3.5 cm o.d. tube connected to 7 cm diameter bulb reservoir attached to 30 cm long X 3 cm o.d. column with 2.5 cm tip on the bottom).
- TurboVap Evaporator and tubes, Zymark Ltd., Mississauga, Ontario.

Method

For each sample or replicate:

1. The weight of the aluminum weighing boats for each determination is measured and recorded.
2. 5 g of each sample is weighed accurately into a pre-weighed weighing boat.
3. Each sample is transferred quantitatively to a mortar with 100 g of anhydrous sodium sulfate. The mixture is ground until it is homogeneous and then transferred to a glass extraction column. The column is packed with glass wool at the tip and a TurboVap sample tube is placed under the column. The aluminum weighing boat, mortar and pestle, funnel and spatula are rinsed three times with 1:1 dichloromethane:hexane. The column is eluted with 100 mL of 1:1 dichloromethane:hexane. The solvent is reduced to 1 mL approximately in the TurboVap and then quantitatively transferred with 1:1 dichloromethane:hexane to another pre-weighed aluminum weighing boat.
4. The weighing boat and solvent are dried in a 40 °C vented oven for several hours or overnight. The samples are cooled completely in a desiccator over anhydrous calcium sulfate and then their weights are measured and recorded (yields the weight of lipid).
5. Percent lipid is calculated using the following equation:

$$\frac{\text{Weight lipid} \times 100\%}{\text{Weight sample}}$$

Notes: each batch of samples is to be organised as follows
1 CRM
1 replicate
6 to 8 samples

LIPID DETERMINATION FOR MICROSAMPLES AND OTHER UNIQUE SAMPLES

Certain types of samples, such as marine mammal biopsy darts or other unique samples, necessitate determination of lipid amount from the same sample extract used for contaminant determination. In the case of samples used in gram quantities, the 500 mL flask used to collect the original extract is pre-weighed and the weight recorded. The sample is rotary evaporated as per the normal procedure but before gel permeation chromatography, the sample is allowed to go to dryness in a fume hood. The flask plus lipid is then weighed to allow calculation of the lipid weight by difference.

In the case of microsamples (mg quantities of sample), the sample is rotary evaporated after initial extraction and then transferred into a pre-weighed glass centrifuge tube. It is then allowed to go to dryness in a fume hood. The centrifuge tube is useful because it allows the sample to be coated on the walls of the tube to facilitate solvent evaporation.

SAMPLE PREPARATION AND CLEAN UP FOR PCDD/F, PCB, PBDE AND PCDE ANALYSIS

1. TISSUE

A. Extraction

The general principles behind this procedure are to:

1. Remove all water from the sample so that
2. All organic, lipid-soluble materials may be extracted.
3. The sample is then put through a series of clean up steps to isolate the compounds of interest:
   a. Gel permeation chromatography; to remove larger lipid molecules. Microsamples and samples with very low lipid percentages (<1% lipid by weight) are not processed through gel permeation chromatography; they proceed to silica chromatography following extraction. Silica chromatography removes small amounts of lipid from these samples adequately.
   b. Silica chromatography; to oxidise, polymerise sample matrix and retain it on the silica column
   c. Alumina chromatography; to further remove non-target compounds and matrix by fractionation.
4. The final step in the process is carbon fibre chromatography. This part of the procedure fractionates compounds in the sample based on size, degree of halogenation, and planarity.

All samples are spiked with surrogate internal standard before extraction begins. Each sample fraction is spiked with surrogate recovery standard at the end of the cleanup and fractionation steps. The RDL uses surrogate compounds for all of its internal and recovery standard cocktails, as part of the isotope dilution method of sample preparation and analysis.

A surrogate compound is one that is the same as a compound of interest except that it has a unique isotopic composition. For instance, the surrogate internal standard for 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) has its entire carbon skeleton as ^{13}C, the heavy (not radioactive) isotope of carbon. Carbon in "native" compounds, or those compounds found in the environment, are predominantly ^{12}C. One advantage of this approach is that internal surrogate compounds will elute at the same time as the native compound, allowing retention time matching for identification purposes. The other useful property of a surrogate internal standard is that it is also processed through all of the cleanup and fractionation steps. The surrogate internal standard is lost to the same extent through the clean up process relative to the matching native compound. This allows calculation of "unknown" amount of native compounds compared against the "known" amount of their surrogate internal standard. Equations for quantification of

native compounds and recoveries of surrogate internal standards may be found in Appendix V.

The extraction, clean up and analytical methods were validated, as per Huang et al. 1992, by extracting and then analysing:

1. *Fortified samples.*
   Fortified samples of fish were prepared by spiking PCDD/F standards at different concentrations. Samples were then extracted and analysed. For all congeners analysed, a >10 % relative standard deviation (RSD) was obtained.

2. *Method blanks.*
   Repeated injections of method blanks did not contain measurable levels of any of the congeners.

3. *Field samples.*
   The criteria for identifying and quantifying all congeners are outlined in the Instrumental Analysis section, parts D. Qualitative determination. Criteria for Positive Identification. and E. Quantitative determination.

Materials

- Sodium sulfate: anhydrous, granular sodium sulfate (Mallinckrodt Baker, Inc., Paris, Kentucky) baked at 450 ^{0}C at least overnight and cooled to room temperature in a desiccating chamber.
- 1:1 DCM:hexane (both solvents pesticide residue analysis grade, Caledon Laboratories Ltd., Georgetown, Ontario).

Equipment

- Porcelain mortar, 750 mL capacity, (Coors, Golden, CO).
- Porcelain pestle, 215 mm length, (Coors, Golden, CO).
- Extraction reservoir: 24/49 ground glass joint (female)
  500 mL round bottom flask
  4 mm Teflon™ stopcock
  24/49 ground glass joint (male)
- Extraction column: 24/49 ground glass joint (female)
  35 cm long
  ~35 cm o.d.
  4 mm Teflon™ stopcock
  glass tip
- Large powder funnels (100 mm i.d. top, 18 mm o.d. stem) (Kimble Glass, Vineland, New Jersey, U.S.A.).

Method

a. Each thawed sample is mixed before weighing to ensure homogeneity.
b. Approximately 10 g of wet sample is weighed into a tared weighing boat; sample weight is recorded to at least two decimal places.
c. With each batch prepare a procedural blank: 0.15 g of triolein (95%, Sigma-Aldrich, Canada, Ltd., Oakville, Ontario). This blank is processed using the same procedures as the samples.
d. Surrogate internal standard(s) are then spiked onto weighed tissue or blank sample. Appendix I lists spiking amounts for PCDD/Fs, PCBs, PCDEs and PBDEs.
e. Each spiked sample or blank is ground in a large mortar and pestle with 200 g sodium sulfate until a free-flowing mixture is attained.
f. The sample mixture is transferred to an extraction column quantitatively with rinses of 1:1 dichloromethane:hexane. The balance of 1:1 dichloromethane:hexane is added to an extraction reservoir such that approximately 350 mL of solvent has been passed through the column. The reservoir is placed on top of extraction column and the column is eluted into a 500 mL round bottom flask.
g. The sample volume is reduced to a few mL by rotary evaporation. The sample is then dissolved in about 5 mL of 1:1 DCM:hexane to assure correct solvent composition for gel permeation chromatography.

B. Gel Permeation Chromatography

Gel permeation chromatography (GPC), or, size exclusion chromatography, is a technique used to separate molecules on the basis of size. The RDL uses GPC to selectively retain the smaller size fraction of the sample while discarding the larger molecular weight portion of the sample. It is important to develop "cut points" for all chromatography columns based on the exact volume of the stationary phase (Biobeads, in this case) and type of mobile phase used.

Materials

- 70 g of Biobeads S-X3 (Bio-Rad Laboratories (Canada) Ltd., Mississauga, Ontario).
- 1:1 DCM:hexane (both solvents pesticide residue analysis grade, Caledon Laboratories Ltd., Georgetown, Ontario).

Equipment

- gel permeation column: 24/29 female ground glass joint
  55 cm long X ~3.5 cm o.d. column
  coarse glass frit

4mm Teflon™ cone stopcock
glass tip

Method

a. Biobeads are swelled in 1:1 DCM:hexane for at least 24 hours. The Biobeads are then slurry-packed into the gel permeation column. A head of 1:1 DCM:hexane is maintained on the column at all times while the column is being stored. If the column goes dry, the beads will need to swell in 1:1 DCM:hexane before the column is used. A column that has gone dry and has developed air pockets or cracks in the bead layering will need to be swelled in solvent and then repacked.

b. Concentrated samples will occasionally be cloudy or there will be particulate matter observed in the concentrated samples. These particulates are attributed to the limited solubility of polar lipids in 1:1 DCM:hexane and seems to occur most often with crab hepatopancreas samples. It is then necessary to filter the concentrated sample through a non-sterile Millex-SR 0.5 μm disposable syringe filter (Millipore (Canada), Ltd., Nepean, Ontario). The concentrated sample is drawn into a clean, 10 mL gastight syringe with a Luer lock end fitting. A syringe filter is then attached to the end of syringe. The sample is expelled, gently, back into the sample flask. This process may require more than one syringe filter. Filters are replaced immediately if they become plugged. All transfers should completed as quantitatively as possible.

c. The extracted, concentrated sample is added quantitatively, in 1:1 DCM:hexane, to the top of the GPC column. The sample must migrate well onto the head of the column and the top of column must not go dry. The solvent volume required to add the sample to the column is then recorded and this "load" volume discarded. 500 mL of 1:1 DCM:hexane is added to the top of the column. The column flow rate should be approximately 5 mL min^{-1}. An additional (dump) volume of solvent is collected such that the total load plus dump is less than or equal to 140 mL. The dump volume is discarded. Into a 500 mL round bottom flask collect approximately an additional 350 mL. The sample is reduced in volume to about 2 – 5 mL by rotary evaporation.

d. GPC columns are rinsed with approximately 350 mL 1:1 DCM:hexane after use. Stopcocks are changed between samples and the interior surfaces of the column below the glass frit as well as the exterior surface of the glass tip are rinsed well with 1:1 DCM:hexane.

e. One GPC standard is run after each batch of samples on the columns. The standard consists of approximately 0.15 g triolein weighed into a 15 mL glass centrifuge tube and spiked with dioxin/furan and PCB surrogate internal standards (see Appendix I).

C. Acidic/Basic Silica Chromatography

Silica chromatography is one of standard types of sample preparative tools in the preparative chemists' tool kit. This particular type of silica column uses the oxidative power of concentrated sulfuric acid to remove polar lipid from the sample. Silica gel (silicic acid) is also weakly acidic so it will retain polar matrix components (Anon. 1996b). Larger volume (5X and 10X) silica columns are used specifically for highly coloured samples such as sediment and fly ash. Biota samples, such as crab hepatopancreas, will occasionally require two single volume silica columns to render the sample colourless.

Materials

- Neutral Silica: 100-200 mesh silica (Mallinckrodt Baker, Inc., Paris, Kentucky). Activated, at least overnight, at 200 ^{0}C and then cooled to room temperature in a desiccating chamber over anhydrous calcium sulfate.
- Sulfuric acid: ACS assured grade (BDH Inc., Toronto, Ontario).
- Toluene-washed water: Milli-RX 20-processed water (15 megohm-cm, 50 ppb total organic carbon (Millipore (Canada), Ltd., Nepean, Ontario).) washed twice with toluene (pesticide residue analysis grade, Caledon Laboratories Ltd., Georgetown, Ontario).
- Acidic Silica: 25.0 g concentrated sulfuric acid added to 50 g of neutral silica and shaken to a free-flowing powder.
- Basic Silica: 14.0 g of 1 N sodium hydroxide (made up with toluene-washed water) added to 40 g of neutral silica and shaken to a free-flowing powder.

Note: silica used for a maximum of three days after activation and then a new batch must be prepared.

- 1:1 DCM:hexane (both solvents pesticide residue analysis grade, Caledon Laboratories Ltd., Georgetown, Ontario).

Equipment

- 40 cm custom glass column with reservoir: -30 cm long X 12 mm o.d. X 10 mm i.d
  -100 mL reservoir
  -10 mm o.d. coarse glass fritted plug end (8 mm i.d.).
  -straight bore Teflon™ stopcock and burette tip (Kimble Glass Inc., Vineland, New Jersey, U.S.A.).

Method

The following amounts of prepared silica are dry packed in layers into the column in the following order (bottom layer first) for a single volume column:
1. 2 g basic

2. 1 g neutral
3. 4 g acidic
4. 1 g neutral

Larger columns (5X and 10X) are simply extrapolated from this basic recipe.

a. The column is rinsed with 50 mL 1:1 DCM:hexane and then the sample is added quantitatively. The sample is eluted with 60 mL 1:1 DCM:hexane and collected into a 250 mL round bottom flask. Additional silica columns are run if the acidic layer is saturated with colour.
b. The stopcock and tip used for silica chromatography is retained, labelled with sample identification, for use in alumina chromatography.

D. Alumina Chromatography

Alumina is another conventional chromatographic clean up tool. It is a highly porous and granular form of aluminum oxide. This method uses neutral alumina (pH 6 – 8) but it is also available in a basic (pH 9 – 10) or acidic (pH 4 –5) form. Neutral alumina is used to separate compounds such as aldehydes, ketones, quinones, esters, lactones and glycosides (Anon. 1996a). All types of alumina are used to separate compounds of interest from interfering materials based upon differing chemical polarities.

Materials

- Alumina: neutral alumina, super I activity, (ICN Biomedicals, Eschwege, Germany) activated at 200 ^{0}C at least overnight and cooled to room temperature in a desiccating chamber.
- Sodium Sulfate: anhydrous sodium sulfate (granular, Mallinckrodt Baker, Inc., Paris Kentucky) is baked at 450 ^{0}C at least overnight and cooled to room temperature in a desiccating chamber over anhydrous calcium sulfate.
- Hexane
- 1:1 DCM:hexane
(all solvents pesticide residue analysis grade, Caledon Laboratories Ltd., Georgetown, Ontario).

Equipment

- 40 cm custom glass column with reservoir: -30 cm long X 12 mm o.d. X 10 mm i.d
-100 mL reservoir
-10 mm o.d. coarse glass frit and plug end (8 mm i.d.)
-straight bore Teflon™ stopcock and burette tip (Kimble Glass Inc., Vineland, New Jersey, U.S.A.).

Method

a. The column is dry-packed with 10 g activated alumina followed by 1 g sodium sulfate. The column is then rinsed with 25 mL of hexane. The sample is taken to near dryness by rotary evaporation after it has been processed through acidic/basic silica cleanup. Allow sample to go to complete dryness at room temperature. The sample is then dissolved in a few mL of hexane.
b. The sample is added, quantitatively, to the top of the alumina column with hexane. 25 mL of hexane is passed through the column. This hexane wash of the sample is collected into a labelled scintillation vial. This wash is known as the "hexane fraction" and is stored, labelled with the sample i.d., in the freezer until after all PCB and PCDD/F analyses are complete.
c. 60 mL 1:1 DCM:hexane is passed through the column and collected into a 250 mL round bottom flask. This is the sample fraction.

E. Carbon Fibre Chromatography

Carbon fibre chromatography is used to fractionate the prepared sample into four fractions:

1. Fraction I: contains di/tri/tetra-ortho-substituted PCBs (DO-PCBs).
2. Fraction II: contains mono-ortho-substituted PCBs (MO-PCBs).
3. Fraction III: contains non-ortho-substituted PCBs (NO-PCBs).
4. Fraction IV: contains PCDD/Fs.

This fractionation is not an absolute process; there is variable elution of some of the di- and tri-substituted DO-PCBs between Fractions I and II. PCB 169 (a NO-PCB) also fractionates in an unpredictable fashion between Fractions III and IV. To compensate for the nature of these fractionations, the problematic di- and tri-substituted DO-PCBs are quantified in both Fractions I and II. The concentrations are then determined based on whichever fraction had best recovery of the surrogate ($^{13}C_{12}$-PCB 28). Fractions III and IV are combined before analysis for NO-PCBs. One further variable is added for the analysis PBDEs: these compounds elute over the range of Fractions I through IV. Therefore, in cases where a single sample is analysed for PCDD/Fs, all 209 PCBs, and PBDEs, the following analysis schedule must be followed:

1. Analyse Fraction I for DO-PCBs
2. Analyse Fraction II for MO-PCBs
3. Analyse Fraction IV for PCDD/Fs
4. Analyse Fraction III/IV combination for NO-PCBs
5. Analyse Fraction I/II/III/IV combination for PBDEs.

Samples to be analysed for PCDEs must be a combination of Fractions I, II, and III.

Additional analyses of the combined fractions for analytes/fraction combinations not listed above will likely compromise data quality due to:

a. PCDEs in Fraction III, which may interfere with the analysis of PCDFs
b. Coeluting PCBs, which in fractionated samples are separated (occurs in any combination of Fractions I, II, and III0
c. Matrix interferences, eluting primarily in Fraction I.

Materials

I. Solvent

The four solvents and mixtures of solvents are:

1. Solvent 1 = 3% dichloromethane in hexane
2. Solvent 2 = 50:50 dichloromethane in cyclohexane
3. Solvent 3 = 50:50 ethyl acetate:benzene
4. Solvent 4 = toluene

All solvent mixtures are stirred for at least 2 hours using a magnetic stirrer and then transferred to marked 4 L brown solvent bottles for storage until use. Solvents are transferred into one liter narrow mouth bottles for use with the carbon fibre system. Care should be taken to keep solvent levels above the level of the inlet filters in the bottles. Solvent 1 should be made and changed daily when the instrument is in use to ensure constant composition. The other three solvents or solvent mixtures maintain acceptably constant composition over time when the instrument is being used frequently.

Sample fractions are eluted using the following solvent profile:

Fraction	Time (minutes)	Flow rate (mL minute-1)	Direction of flow
I	10	2	forward
II	11	2	forward
III	25	2	forward
IV	15	4	backflush

II. Carbon fibre columns

Columns are packed by hand and then each column is conditioned before use by running 4 solvent cycles throughout the carbon fibre system. Two columns may be made with the amount of packing material listed below. It is not advisable to store unused packing material.

- 600 mg glass filter paper (124 mm P100 prefilter sn. 211707 (Nucleopore Corp., Pleasanton, CA) cut or torn into small pieces

- 50 mg PX-21 carbon (BP Amoco Chemicals, Naperville, Illinois)

The filter paper and carbon are combined in a long narrow beaker, Erlenmeyer or large test tube. Bearings at the bottom of the Brinkmann/KINEMATICA POLYTRON PT 10/35 homogenizer probe (Brinkmann Instruments, Inc., Westbury, NY) must be submerged in solvent while the probe is running. 50 - 100 mL of dichloromethane is added and the mixture is homogenized until there are no large lumps of filter paper left.

Equipment

- all Waters (Waters, Ltd., Milford, MA) liquid chromatography equipment:
  590 Programmable HPLC pump
  SSV Solvent Select Valve
  U6K injector
  Automated Switching Valve
- Carbon/glass fibre column (as described in method section following)
- 2 mL gas-tight syringe with Teflon™ Luer lock end and needle to fit U6K injector
- 10 mL gas-tight syringe with Teflon™ Luer lock end and end fitting for 590 pump purge port.

Method

I. Column assembly

- 7.5 cm long X 7 mm o.d. X 5 mm i.d. stainless steel tubing
- stainless steel low volume reducing unions, equipped with 2.0 micron stainless steel frits and 1/4" i.d. ferrules and stainless steel distributors

All columns and fittings should be ultrasonicated in dichloromethane prior to use. One fitting is assembled, attached to one end of the column and then the column is suspended over a beaker with the attached fitting on the bottom. The carbon fibre material is packed into the column with a small stainless steel scoop and glass pipette. Small quantities of packing material are used and pushed down into the bottom of the column, packing firmly but not extremely tightly. Once the packing material is level with the top of the column the second fitting may be attached. The column is now ready for installation. The prepared column may be stored in freezer until use, labelled with the preparation date.

II. Standards

A standard solution of dioxins, furans, and PCBs is then run to document recoveries and fractionation. Standards are also run after 30 samples have been put through each column.

III. Flow Testing

The flow rate for each fraction elution step from each newly installed column is documented in the carbon fibre flow rate log. The flow rates are documented periodically over the life of the columns.

IV. Purge procedure

a. A small amount of hexane is dripped into the barrel of the 10 mL gastight syringe to lubricate the plunger.
b. All solvent bottles need now to have adequate levels of solvents.
c. Solvent 1 (3% dichloromethane in hexane) must be emptied and then refilled with freshly made solvent.
d. Nitrogen cylinder must be turned on and set to about 40 psi.
e. Pump is turned on (switch at lower right of pump).
f. Pump is in manual mode (selected by entering <2nd function><manual>).
g. Solvent select valve (SSV) is switched from "auto" to "manual".
h. Solvent 4 (toluene) is selected manually on the SSV. The 10 mL gastight syringe is inserted into the Teflon™ pump's purge port, the knurled ball valve is opened several turns and solvent is withdrawn until the syringe is full of solvent. The knurled ball valve is closed and the solvent in the syringe is expelled to waste. This procedure is repeated until all bubbles are removed from the solvent line.
i. Step 7 is repeated for any solvents with air in the lines. This should only really be necessary for 1:1 DCM:cyclohexane and 3% DCM in hexane when the system is being used fairly frequently. All lines coming into the Waters 590 pump MUST be filled with Solvent 1 (3% DCM in hexane) before proceeding.
j. Solvent 1 is selected on the SSV. The reference valve is opened by turning the grey switch above the pump's pistons to the right until it is loose. A few mL of solvent is then drawn into the syringe. There must be a waste container under the 2 front solvent delivery ports. A high flow rate (7 - 10 mL per minute) is then entered into the pump by entering <numeric value><enter>. Air bubbles in the pump are pushed out by pressing firmly on the syringe plunger. As soon as there is a constant solvent flow from the appropriate solvent delivery port, the reference valve is closed by turning it to the left until it is snug. The knurled ball valve is closed and the syringe is withdrawn from the purge port. A flow rate of zero mL per minute is now entered into the pump and then the SSV may be then switched from "manual" to "auto".

The system is ready to use.

- This procedure above needs to be carried out every day before samples are run.
- After the system is purged, Solvent 1 must be run for a few minutes at 2 - 4 mL per minute through the column to equilibrate it to initial conditions for the solvent cycle.

- The solvent lines must be monitored for bubbles periodically during a sample run. Bubbles can enter the pump and may affect flow rates and subsequently affect fractionation.

V. HPLC Injector cleaning and injection procedure

a. The injector lever is rotated to "load" and the pin is withdrawn from the injection port.
b. The pin is sonicated with a few volumes of toluene.
c. The injector port is rinsed with 5 - 6 mL of toluene, followed by 5 – 6 mL of dichloromethane, followed by 5 - 6 mL of hexane. 5 - 6 mL of clean hexane is pushed through the injection loop.
d. Excess solvent is removed from the port with the syringe.
e. With hexane-lubricated clean syringe, sample is drawn into the syringe.
f. A small volume of hexane is added to the sample container and the container is rinsed using a disposable Pasteur pipette. This wash is drawn into the sample syringe. The is procedure is repeated 2 - 3 times while keeping the total volume less than or equal to maximum syringe volume.
g. Excess air is expelled from the syringe carefully, if necessary.
h. The syringe needle is inserted into the port and the sample is injected. Solvent will flow from the loop into the small waste bottle on the front of the injector.
i. 0.1 - 0.2 mL of hexane is drawn into the syringe and the plunger is pulled to maximum volume of syringe. Excess air is expelled. This wash is injected with two more repetitions so that the syringe has effectively been rinsed three times. Total volume that is added to the injection loop MUST be less than 2.0 mL. The loop volume is 2.0 mL.
j. The injection port pin is inserted into the port and rotate lever to "inject" position.
k. The system is started by pushing <1><second function><enter>.

VI. Troubleshooting Guide

- Symptom: solvent pulsing out of the column outlet rather than coming out at a constant flow rate.
- Problem: air bubble in the pump.
- Solution: if a sample is being run and the run has progressed farther than the first fraction, recover all fractions, recombine them, concentrate them and put the sample through the carbon fibre system again. Fraction volumes are important but not extremely critical. If a sample is being run but the fraction volume(s) have not been compromised substantially, attach the purge syringe to its port, draw out a volume of the solvent, and push solvent through the pump until the flow appears constant. This should all take less than one minute.

- Symptom: no solvent flowing into the waste container when an injection is made and sample leaks out of the injection port while the injection is being made.
- Problem: defective injector needle seal or injection technique.

- Solution: Ensure that injection technique is correct. If the injection is being made correctly, the Teflon™ needle seal needs to be changed. Consult the Water's operator's manual and change the needle seal. Spare parts are kept in the cupboard under the rotary evaporators. The injector area may be contaminated so be sure to wear gloves and thoroughly solvent rinse the port when the seal once the changed.

- Symptom: low flow rate, low pressure or no flow.
- Problem: air bubbles in the pump, leaks in the lines or solvent bottles empty.
- Solution: Check all of the column connections and switching valve connections for leaks. Ensure that the reference valve is close. Purge pump of bubbles. Check solvent bottle levels.

- Symptom: incorrect solvent flow direction or switching valve does not switch column flow direction at programmed time.
- Problem: the compressed gas line has become disconnected or the tank is empty or not on.
- Solution: reconnect, replace, or turn on as necessary.
- Solution: this problem can require more complicated procedures to correct fractionation or to recover a sample.

- Symptom: single solvent is being delivered through the column during the entire run.
- Problem: the solvent select valve is on "manual".
- Solution: switch the solvent select valve to "auto".

- Symptom: entering <1><2nd function><enter> does not start automated sequence.
- Problem: dead memory battery in pump.
- Solution: re-enter program steps and check carefully. Do not turn pump off again until battery is available. Have a person from the electronics section install the battery into the pump's main electronic board.

Note: if any of the previous problems cannot be solved with aid from this guide or from the troubleshooting guide in the Waters Model 590 Programmable Solvent Delivery Module Operator's Manual, call the service representative for advice. Log the service problem at 1-800-252-4752 extension 8180. This number is in Maryland (+3 hour time difference).

VII. Sample Fraction Preparation for Analysis

Sample fractions are evaporated down to minimum volume on rotary evaporator. Each sample fraction is then transferred into a glass centrifuge tube and evaporated under a stream of nitrogen to 0.1 to 0.3 mL. The sample fraction is transferred into a pre-labelled amber microvial with toluene and evaporated, if necessary, to a

reduced volume under a stream of nitrogen. The chart below is used as a guide to final fraction volumes for specific sample types. The surrogate recovery standard(s) is (are) added and the microvial capped with an aluminum crimp seal with septum. Each sample vial is vortexed. The fraction is ready for analysis. **Final vial volume to be recorded in the appropriate batch booklet table**.

VIII. Final Vial Volumes for Analysis

Sample Type	Code	Fraction	Approximate Final Vial Volume (µL)
Incinerator/XAD2	I	Fr I	300
		Fr II	50
		Fr III	50
		Fr IV	50
Tissue	A / B	Fr I	25
		Fr II	100
		Fr III	25
		Fr IV	25
Killer Whale Darts	F	Fr I	600
		Fr II	600
		Fr III	25
		Fr IV	25
Seal Blubber	F	Fr I	600
		Fr II	250
		Fr III	50
		Fr IV	25
Hepatopancreas	H	Fr I	50
		Fr II	600
		Fr III	50
		Fr IV	50
Liver	L	Fr I	600
		Fr II	300-400
		Fr III	50
		Fr IV	50
Sediment	S	Fr I	50
		Fr II	50
		Fr III	25 - 50
		Fr IV	25 - 50
Lake Trout CRM	T-CRM	Fr I	600
		Fr II	600
		Fr III	50
		Fr IV	50
Milk	M	Fr I	600
		Fr II	25
		Fr III	25
		Fr IV	25
Glass (not fractionated)	Glass		50

F. Silver Nitrate Chromatography

Fraction I generally contains the highest concentration of potentially analytically-interfering compounds of any of the fractions generated from carbon fibre chromatography. These interferences can be so severe that reliable quantification of compounds in Fraction I or in any combination of fractions containing Fraction I may be compromised. Silver nitrate columns are used to further clean up Fraction I of samples that are routinely problematic, i.e. fly ash, sediment, incinerator, and also for Fraction I that are found to be problematic after first analysis. It is preferable to put suspected "dirty" Fraction I of samples through silver before addition of surrogate recovery standard.

Materials

- Activated Silica: 100-200 mesh silica (Mallinckrodt Baker, Inc., Paris, Kentucky) is activated, at least overnight, at 200 ^{0}C and then cooled to room temperature in a desiccating chamber over anhydrous calcium sulfate.
- Silver nitrate (BDH Inc., Toronto, Ontario) AnalaR grade, 99.8% minimum assay.
- Reverse osmosis-processed (RO) water. 15.0 MΩcm product.
- sodium sulfate: anhydrous, granular sodium sulfate (Mallinckrodt Baker, Inc., Paris, Kentucky) is baked at 450 ^{0}C at least overnight and cooled to room temperature in a desiccating chamber over anhydrous calcium sulfate.

Equipment

- 40 cm custom glass column with reservoir: -30 cm long X 12 mm o.d. X 10 mm i.d
  -100 mL reservoir
  -10 mm o.d. coarse glass frit and plug end (8 mm i.d.)
  -straight bore Teflon™ stopcock and burette tip (Kimble Glass Inc., Vineland, NJ).

Method

10% Silver nitrate coated silica:

It is absolutely necessary that the silver nitrated coated silica be prepared one day in advance of running the silver columns. The Environment Canada method (Anon. 1992), with some slight modifications, is followed. Amounts of silver nitrate and silica used are adjusted to 2 g per column. Silver nitrate is very expensive ($370/100g) and very environmentally unfriendly – so as little as possible is used. The beaker / spatula used to make the acid solution is rinsed into the silver nitrate waste bottle before putting it into the wash cycle.

1. 5.6 g of silver nitrate is dissolved into 21.5 mL RO-water. This solution is then added, in a stepwise manner, to 50 g of cooled, activated silica in a glass-stoppered flask. Between additions, the flask is shaken until a uniformly-coated free-flowing powder is produced. When all silver nitrate has been added, the material is allowed to stand for approximately 30 minutes. The mouth of the flask is then covered with solvent-rinsed aluminum foil and placed in an oven at 30°C. Over a five-hour period, the oven temperature is gradually increased to 120 °C and conditioning continues overnight at this temperature. The mixture is cooled to room temperature and the flask is wrapped immediately with aluminum foil. Exposure to of this material to light should be minimised. The mixture is stored in a dessicator until use. This material has a life of one day; extra material is discarded into the silver nitrate waste container.
2. Columns:
   a. All samples need to be free of dichloromethane and then dissolved in hexane. 2.0g of 10% $AgNO_3/SiO_2$ is added to the silica column and a 1-2 cm layer of sodium sulfate is added on top. The portion of the column containing the $AgNO_3$ is wrapped with foil.
   b. The column is conditioned with 25 mL hexane.
   c. The sample is added to column in hexane.
   d. The column is eluted with 60 mL hexane into a round bottom flask.
3. The sample is reduced in volume to a few mL by rotary evaporation.

G. Extraction Laboratory Schedule for Tissue Samples

The laboratory is provided with a batch of 10 samples plus a certified reference material (CRM). Samples provided to the extraction lab are homogenised or prepared by RDL staff or clients such that they are ready for extraction. Out of these 10 samples one is a replicate, i.e. a second sample from the same original sample, randomly selected. The extraction proceeds as follows:

Day 1 Extraction of **12 samples**:
- 9 real samples
- 1 replicate sample
- 1 CRM
- 1 procedural blank

Day 2 Process samples through gel permeation chromatography (GPC) columns.

Day 3 Process samples through acidic/basic silica columns.

Day 4 Process samples through alumina columns.

Day 5 Process 8 samples through carbon fibre chromatography.

Day 6 Process remaining 4 samples through carbon fibre chromatography and transfer fractions from all samples into amber vials; spike with surrogate recovery standard.

Day 7 Complete the transfers of all sample fractions into amber vials and surrogate recovery standard spiking. Samples are ready for HRGC/HRMS analysis.

Additional samples prepared for HRGC/HRMS analysis include:

- 1 blank sample, spiked with surrogate internal standards, per tissue batch to check GPC column performance and any sample-to-sample cross-contamination.
- Occasional blank samples, spiked with surrogate internal standards, to check the carbon fibre step.
- 1 solvent rinse of glassware (glassware proof) per batch of extracted samples.

The sample preparation lab is currently capable of processing a total of 14 samples every seven single-person working days of the composition/configuration indicated above.

2. SEDIMENT

Chlorinated and brominated organic molecules bind very strongly to organic carbon in sediment samples so repeated solvent extraction is required. Soxhlet processing allows repeated room-temperature extraction of sediment samples and can be left to run overnight once distillation begins.

Materials

- Sodium sulfate: anhydrous, granular (Mallinckrodt Baker, Inc., Paris, Kentucky) baked at 450 ^{0}C at least overnight and cooled to room temperature in a desiccating chamber.
- Solvent-rinsed glass wool.
- 80:20 toluene:acetone (all solvents Omnisolv® grade, EM Science, Darmstadt, Germany)
- high purity water (Omnisolv® grade, EM Science, Darmstadt, Germany) washed twice with toluene
- 1M KOH (87.6%, Sigma Chemical Co., St. Louis, MO, USA) made up with toluene-washed water
- concentrated sulfuric acid (GR grade, EM Science, Darmstadt, Germany)
- sodium chloride (ACS grade, EM Science, Gibbstown, N.J.)
- 1 M HCl (ACS assured grade, BDH, Toronto, ON)
- 10-40 mesh copper (99.9% reagent grade, Aldrich Chemical Co., Milwaukee, WI, USA)
- reagents for silica chromatography
- reagents for alumina chromatography
- reagents for carbon fibre chromatography
- reagents for silver nitrate chromatography

Equipment

- Porcelain mortars, 750 mL capacity, (Coors, Golden, CO).
- Porcelain pestles, 215 mm length, (Coors, Golden, CO).
- Soxhlet extraction tubes (55/50 top joint, 24/40 bottom joint) (Corning Inc., Acton, MA).
- Extraction thimble (45 X 130 mm) with coarse (40 - 60 μm pore size) glass frit (Corning Inc., Acton, MA).
- Separatory funnels (500 mL or 1000 mL) with Teflon™ stopcock and penny-head stopper (Kimble Glass, Vineland, New Jersey, U.S.A.)
- Large powder funnels (100 mm i.d. top, 18 mm o.d. stem) (Kimble Glass, Vineland, New Jersey, U.S.A.).
- 500 mL round bottom flask (Kimble Glass, Vineland, New Jersey, U.S.A.).
- equipment for silica chromatography
- equipment for alumina chromatography

- equipment for carbon fibre chromatography
- equipment for silver nitrate chromatography

Method

I. Soxhlet Extraction

Samples may be organised into batches of 6 or 12. In each batch there must a procedural blank and a replicate sample. The samples are soxhlet extracted in sets of 6 (i.e., if it is a 12 sample batch then there will be two rounds of extractions).

a. Each sample is placed into a solvent-rinsed beaker in case the sample jar breaks while thawing. Samples are allowed thaw at room temperature and then mixed thoroughly. 10 g of each sample is weighed out for the extraction and the weight is recorded. An additional 2 g is required for moisture analysis (one sample in replicate); see also moisture determination procedure in the general sample preparation section of this manual.
b. A glass thimble is prepared by putting a layer of solvent-rinsed glass wool on top of the glass frit. Each 10 g sample is transferred, with 100 g of sodium sulfate, to a mortar and pestle. The mixture is ground until all small lumps are pulverised and a free-flowing consistency is attained. The sample mixture is transferred to the prepared glass thimble in a soxhlet extractor and then 80:20 toluene acetone is used to rinse the mortar, pestle, weighing boat, spatulas and funnels into the extractor. The procedural blank consists of 100 g of sodium sulfate that is placed directly in a thimble. Funnels are retained (labelled with sample identification) for use in transfers until silica chromatography is complete.
c. Surrogate internal standards are added to each sample and to the procedural blank.
d. Sufficient toluene:acetone is added to fill each round bottom flask to about 2/3 full (300-350 mL).
e. Each sample is soxhlet extracted for about 17 hours such that the turnover rate is about once every 20 minutes. Each sample is allowed to cool to room temperature.

II. Base and Acid Wash

The next steps involve multiple washes of the sample. To save on the volume of glassware needed it is helpful to retain each set of (labelled) separatory funnels, and 500 mL round bottom flasks (and the funnels, as noted previously) until silica chromatography is complete. It is also useful to rinse the round bottom flasks with one or two aliquots of acetone between each use. This will remove glass wool and sodium sulfate particles that may cause bumping on the rotary evaporator.

a. Each sample is transferred from its round bottom flask to a 500 or 1000 mL separatory funnel. 40 mL 1M KOH is then added to the separatory funnel and the mixture is shaken for 2 minutes and then the KOH layer is discarded. The

toluene:acetone layer is then washed with 80 mL high purity water for 2 minutes and the water layer is discarded.

b. 10 mL of concentrated sulfuric acid is added to the separatory funnel and the mixture is shaken for 2 minutes. The acid layer is removed. Acid washing is repeated until sample is colourless. The number of acid washings used for each sample is recorded. The procedural blank is washed with the maximum number of acid washings used for the samples.
c. Approximately 80 mL of high-purity water is added to the separatory funnel and shaken for 2 minutes. The water layer is discarded. This step is repeated two more times. Sodium chloride saturated water is added, if necessary, to break thick emulsions. As much of the water as possible is removed after water washes are complete.
d. Each sample's large powder funnel is prepared by plugging it with solvent-rinsed glass wool or adding a filter. Approximately 100-200 g of sodium sulfate is added to the funnel. The sample is dried by passing it through the prepared funnel and into its round bottom flask. Sample volume is reduced to near dryness by rotary evaporation. The sample is allowed to go to dryness at room temperature such that no toluene remains and the sample is completely dry.
e. Each sample is dissolved in a few mL of 1:1 DCM:hexane.

III. Acidic/basic silica column

a. Each sample is run through a 5X volume silica column (as per protocol in tissue extraction procedure). If the column does not saturate with colour, a 1X volume silica column is run and the sample proceeds to the copper column step. If the 5X column saturates the acid layer with colour, 10X volume columns are run until they do not saturate and the sample then proceeds to 5X or 1X columns.
b. Once the sample no longer saturates the acidic layer of the larger volume silica columns, normal volume columns are run until their acid layer does not saturate. Concentrated samples may be added directly from their 500 mL round bottom flask to larger silica columns. Samples may also be collected into their originating round bottom flask. 5X and 10X volume columns are rinsed with 250 mL 1:1 DCM:hexane before use and the sample is eluted from the column with 300 mL 1:1 DCM:hexane.
c. Each sample is water washed following silica chromatography, as in Base and Acid Wash, step II. (c) above, if 5X or 10X silica columns were used. These water washes are continued until the wash is near neutrality (the wash is tested with pH paper).
d. If the sample has been water washed, it must be dried as in Base and Acid Wash, step II. (d), above. Before passing the sample through the funnel, add a few g of sodium sulfate to the flask and swirl contents well. The sample is taken to near dryness by rotary evaporation.
e. Each sample is allowed to go to complete dryness at room temperature.
f. Each sample is dissolved in a few mL of hexane.

IV. Copper column

For each sample:

a. 5 g of 10-40 mesh copper is placed into a silica/alumina style column without a stopcock and covered with 1 M HCl. The acid is drained away and rinsed thoroughly with toluene-washed water. This water is drained and rinsed thoroughly with acetone. A straight bore PTFE stopcock and burette tip is attached to the column. The acetone is replaced with hexane and a few centimetres of sodium sulfate is added to the top of the column.
b. The sample is loaded on to a copper column with hexane and eluted with 30 mL hexane. The sample is collected into a fresh 125 mL round bottom flask. Additional copper columns must be run if a sample's entire copper column is darkened.
c. The sample is taken to near dryness by rotary evaporation.
d. The sample is allowed to go to complete dryness at room temperature in a fumehood and then dissolved in a few mL of hexane.

V. Alumina, Carbon fibre and Silver nitrate chromatography

a. Alumina chromatography: as per tissue extraction procedure.
b. Carbon fibre chromatography: as per tissue extraction procedure.
c. Silver nitrate chromatography: (for sediment and soil extract Frl's only) as per tissue extraction procedure.

VI. Sediment Moisture determination

See general sample preparation section.

3. MUNICIPAL WASTE INCINERATOR SAMPLES

Sampling trains are used to collect airborne materials from the interior of the incinerator stack. One sampling train yields the following materials for extraction and analysis:

- resin, glass wool, "rinse" and filter
- water / ethylene glycol

Clients sometimes also include pre-extracted samples, which do not require soxhlet extraction.

The extraction and " cleanup " of the resin is based generally on the principles from the EPA Method 23 (Anon. 1995). This extraction protocol is also very similar to that which the Regional Dioxin Laboratory uses for sediment samples.

Materials

- Reagents as for soxhlet extraction and clean up of sediment samples
- 100-200 mesh silica (Mallinckrodt Baker, Inc., Paris, Kentucky) (activated, at least overnight, at 200 ^{0}C and then cooled to room temperature in a desiccating chamber over anhydrous calcium sulfate).

Equipment

- As for soxhlet extraction of sediment samples.

Method

I. Resin, glass wool and filter samples

Resin, glass wool and filter samples are soxhlet extracted.

a. A procedural blank is included as a soxhlet-extracted sample with each set of samples.
b. Resin plus glass wool, rinse and filter are processed together as a single sample. The "rinse" is transferred quantitatively to a 500 mL round bottomed flask which is rotary evaporated to a few millilitres. This flask is used as part of the soxhlet extraction apparatus for the next step.
c. The XAD_2 resin, glass wool and filter are transferred to one or two soxhlet glass thimbles (extra coarse frit and a very thin coating of silica over the frit) depending on the volume of resin received. Each thimble is spiked with appropriate surrogate internal standards.
d. Samples are soxhlet-extracted with 80:20 toluene:acetone overnight.
e. Split samples (i.e. resin samples that were two big to fit into one glass thimble), as extracts, that were split in order to soxhlet extract them are now recombined. These samples are also effectively "double" spiked with surrogate internal standards.
f. All soxhlet-extracted samples, including the procedural blank, are base and then acid washed as per the sediment extraction procedure. It may be necessary to wash ten times or more with sulfuric acid to attain colourlessness. The sample is base washed twice and then washed two to six times with 100 mL water. Base and water washing is near completion when the pH of the water is approximately 6. It is sometimes necessary to use saturated sodium chloride in water to break up emulsions between the sample and water. Water washing is complete when the sample and water are relatively clear and colourless. Each sample is dried by passing it through a large powder funnel that been plugged with glass wool and a layer of anhydrous sodium sulfate.

g. Each sample is collected into a clean 500 mL flask. The sample is then taken to near dryness by rotary evaporation. The sample is allowed to dry completely in the fumehood. Each sample is dissolved in a few mL of 1:1 DCM:hexane.

II. Water / ethylene glycol samples

Solvent-solvent Extraction

a. The water / ethylene glycol sample is transferred to an appropriately sized separatory funnel, spiked with surrogate internal standards, and extracted three times with toluene (the ratio of toluene / water is approximately 200 mL toluene / 1000 mL water). After shaking for a few moments in the separatory funnel, the toluene is transferred through a large powder funnel that has been plugged with glass wool and a layer of anhydrous sodium sulfate.
b. The sample is taken to near dryness by rotary evaporation. Each sample is allowed to go to complete dryness in a fumehood. Each sample is dissolve in a few mL of 1:1 DCM:hexane.

III. Pre-extracted Samples

Samples are spiked with surrogate internal standards, transferred into pre-weighed round bottom flasks and dissolved in toluene. Samples can then be split 50/50 by weight if required (this split is used to save a portion of the sample in the case of a unique or irreplaceable sample which may possibly require re-extraction). Samples are processed starting with acid and base washing.

IV. All Samples

a. Silica chromatography: as per soxhlet extraction for sediment procedure.
b. Copper chromatography: as per soxhlet extraction for sediment procedure.
c. Alumina chromatography: as per tissue extraction procedure.
d. Carbon fibre chromatography: as per tissue extraction procedure.
e. Silver nitrate chromatography (for resin and fly ash extracts Frl's only): as per tissue extraction procedure.

4. MILK, BLOOD, AND SERUM

Materials

- Solvents: Glass distilled dichloromethane, hexane, acetone, toluene (Caledon labs, Ontario)
- Silica: 100-200 mesh (Mallinckrodt Baker, Inc. Paris, Kentucky). Activated at 200°C.
- Sodium sulfate: granular (Mallinckrodt Baker, Inc. Paris, Kentucky). Activated at 450°C, 8 hours.
- Alumina (aluminum oxide): ICN-Super I (neutral) (ICN Biomedicals. Eschwege, Germany). Activated at 200 ^{0}C, 8 hours.

Note: Silica, sodium sulfate and alumina are all cooled to room temperature after activation in a desiccating chamber, over anhydrous calcium sulfate.

- Sodium oxalate: ACS certified grade (Fisher Scientific, New Jersey, U.S.A.).
- Sulphuric acid: ACS assured grade, concentrated H_2SO_4 (BDH Inc. Toronto, Ontario).
- Water: Reverse osmosis-processed (15.0MΩcm) water.
- For milk samples only: reagents for gel permeation chromatography as per tissue extraction procedure.
- Reagents for silica chromatography as per tissue extraction procedure.
- Reagents for alumina chromatography as per tissue extraction procedure.
- Reagents for carbon fibre chromatography as per tissue extraction procedure.

Equipment

- Separatory funnels (500 mL) with Teflon™ stopcock and penny-head stopper (Kimble Glass, Vineland, New Jersey, U.S.A.)
- Large powder funnels (100 mm i.d. top, 18 mm o.d. stem) (Kimble Glass, Vineland, New Jersey, U.S.A.).
- 500 mL beakers (Kimble Glass, Vineland, New Jersey, U.S.A.)
- Equipment for gel permeation, silica, alumina and carbon chromatography

Method

I. Extraction

a. Approximately 50 g of milk, blood, or serum is used and the sample weight is recorded. The sample is spiked with the appropriate surrogate internal standards (see Appendix I).
b. The sample is added to a 500 mL separatory funnel.
c. 200 mL of 2:1 acetone:hexane is added to the separatory funnel. The funnel is shaken, venting as required. The aqueous (bottom) layer is drained into the

labelled beaker and the organic layer is drained into a second, labelled, beaker. The aqueous sample is added back into the separatory funnel.

d. Step 3 is repeated twice more.
e. The aqueous "sample" is discarded or retained as necessary. The aqueous "sample" is retained if the sample is unique (no more sample for a second extraction). The combined organic layers are added back into the separatory funnel and washed twice with 100 mL sodium oxalate saturated water. This step removes polar lipoproteins from the sample. Lipid determinations may be falsely inflated if lipoproteins are not removed from the sample.
f. The organic layer is dried by passing it through a large powder funnel (funnel is plugged with clean glass wool and filled about half full with activated sodium sulfate).

II. GPC chromatography

Milk samples only; as per tissue extraction method. Serum and blood samples are not processed through GPC due to their low lipid content.

III. Silica chromatography

All samples; as per tissue extraction method.

IV. Alumina chromatography

All samples; as per tissue extraction method.

V. Carbon fibre chromatography

All samples, as per tissue extraction method.

SAMPLE PREPARATION AND CLEAN UP FOR PESTICIDE ANALYSIS

TISSUE SAMPLE PREPARATION

Many pesticides are quite volatile just above room temperature and others are acid-labile so pesticide sample preparation procedures usually avoid the use of acids and heat.

Materials

- sodium sulfate: anhydrous sodium sulfate baked at 450 ^{0}C at least overnight and cooled to room temperature in a desiccating chamber
- 1:1 dichloromethane:hexane, pesticide grade
- hexane, pesticide grade
- Florisil: anhydrous 60 –100 mesh Florisil baked at 450 ^{0}C overnight and cooled to room temperature in a desiccating chamber. Deactivated with 1.2% toluene-washed water, by weight, and stored under nitrogen until use.

Equipment

- Porcelain mortar, 750 mL capacity, (Coors, Golden, CO).
- Porcelain pestle, 215 mm length, (Coors, Golden, CO).
- Extraction reservoir
  Specifications: 24/49 ground glass joint (female)
  500 mL round bottom flask
  4 mm Teflon™ stopcock
  24/49 ground glass joint (male)
- Extraction column
  Specifications: 24/49 ground glass joint (female)
  35 cm long
  ~35 cm o.d.
  4 mm Teflon™ stopcock
  glass tip
- Large powder funnels (100 mm i.d. top, 18 mm o.d. stem) (Kimble Glass, Vineland, New Jersey, U.S.A.).
- 500 mL round bottom flasks (24/40 ground glass joint) (Kimble Glass, Vineland, New Jersey, U.S.A.).
- 40 cm custom glass column with reservoir: -30 cm long X 12 mm o.d. X 10 mm i.d
  -100 mL reservoir
  -10 mm o.d. coarse glass frit and plug end (8 mm i.d.)

-straight bore Teflon™ stopcock and burette tip (Kimble Glass Inc., Vineland, New Jersey, U.S.A.).

- 15 mL glass centrifuge tube (Kimble Glass Inc., Vineland, New Jersey, U.S.A.)
- 250 mL round bottom flask (Kimble Glass Inc., Vineland, New Jersey, U.S.A.)

Method

I. Extraction

a. 0.1 – 0.2 g of blubber or a 10 g tissue sample is weighed into a tared weighing boat and the sample weight is recorded. The sample is spiked with non-pesticide surrogate internal standards, as required.
b. The sample is ground to a free-flowing mixture in a 750 mL porcelain mortar and pestle with 200 g sodium sulfate.
c. The sample mixture is transferred to an extraction column quantitatively with rinses of 1:1 dichloromethane:hexane and eluted with 250 - 350 mL 1:1 dichloromethane:hexane into a pre-weighed 500 mL round bottom flask. The total weight of the solution is calculated.
d. 30% of the extract solution by weight is transferred into a 250 mL round bottom flask. The sample is reduced in volume to 5 – 10 mL by rotary evaporation and transferred to a screw cap vial. This "pesticide split" is stored in freezer until pesticide sample clean up is required. The 70% portion of the sample can continue on to PCDD/F, PCB, PBDE, and PCDE (as per specific surrogate internal standard spiking) post-extraction sample preparation procedures. **Any samples that have been or need to be pesticide split must be noted on the sample submission sheet when the samples are submitted for extraction.**

II. Pesticide sample clean up

a. Each pesticide sample is spiked with 40 µL of pesticide surrogate internal standard (see Appendix I) and evaporated to near-dryness under nitrogen using minimal or no heat. The sample is allowed to go to dryness at room temperature. **Samples must be monitored with extreme care so that they do not go to dryness on the nitrogen evaporator and so that they do not stand dry at room temperature**. Each dry sample is dissolved in a few mL of hexane.
b. Florisil columns are prepared by adding 8 g of 1.2% water deactivated Florisil slurry-packed with hexane into fritted column. The solvent on the column is then allowed to drain until is it just above the Florisil bed. The sample is transferred quantitatively with hexane to top of column. The column is eluted with 60 mL 1:1 dichloromethane:hexane into a 125 mL round bottom flask.
c. Sample volume is reduced to 1 – 5 mL by rotary evaporation. The sample

is then transferred to a 15 mL glass centrifuge tube with 1:1 dichloromethane:hexane. Sample volume is reduced to 0.2 mL under nitrogen. The sample is then transferred into an amber microvial and evaporated under nitrogen to approximately 100µL.

d. Surrogate recovery standard is added (see Appendix I), the vial is capped, vortexed and submitted for GC/HRMS analysis.

GLASSWARE CLEANING PROCEDURE

GENERAL CLEANING PROTOCOL

(see specific protocol for all exceptions before proceeding)

All dirty glassware from the lab is rinsed with 1x acetone, 1x toluene, and 1x hexane prior to beginning wash cycle. Glassware from extremely dirty samples, especially fly ash, should be rinsed 1x acetone, 2x toluene, 2x hexane, 2x DCM before beginning wash cycle.

When the glassware is dry it is rinse and then soaked in hot water. Soap is not used. The glassware is scrubbed with brushes if necessary. Teflon™ products, silica/alumina push in tips, thimbles, soxhlets or condensers are not put in the dishwasher.

Soap is not used in dishwasher. Neutralising agent windows in the dishwasher need to be checked periodically. Appropriate dishwasher racks for specific glassware must be used. Before beginning a wash cycle, ensure that there is adequate distilled water (up to tape).

When glassware comes out of the dishwasher, it is rinsed with 1x acetone, 1x toluene, and 1x hexane, discarding all washes. The glassware is then allowed to dry in fumehood.

Glassware is baked overnight (**note exceptions**) (6 hours mechanical timer) in vertical oven at 325 °C. Mortars, pestles, any Teflon™ product and other specific equipment is not baked.

Normal solvent rinsing:

Baked glassware is rinsed with:

3x toluene, discard

3x hexane, discard

3x dichloromethane, discard.

Cover with hexane-rinsed aluminum foil or proceed to proof

To proof glassware for batches, rinse:

3x hexane, discard

3x dichloromethane, discard

1x dichloromethane, and collect. (see below)

Specific cleaning protocols:

Safety note: as per the 'General Cleaning Procedure' it is most important that all glassware rinsed with solvents is left to dry completely in a fumehood before storage.

Mortars and pestles following a tissue extraction: are rinsed 1x acetone, 1x toluene, and 1x hexane, discarding each successive rinse and allowing equipment to dry in a fumehood. Equipment is then washed by hand with brushes + hot water and placed in the dishwasher. Mortars and pestles are then rinsed 1x acetone, 4x toluene, 3x hexane, 3x DCM, and proceed to proof.

Mortars, pestles, glass thimbles following a sediment extraction: are placed in a fumehood, the grinding surfaces of the mortars and pestles and the frit of the glass thimble are covered with concentrated sulfuric acid and allowed to stand for a few minutes. (Acid waste is disposed by putting about 1 L of water into an empty 4 L bottle. The acid is poured into bottle using a funnel. The bottle is labeled clearly as bottle ACID WASTE.) The sink is filled with water and the acid washed items are put into it. (NEVER POUR WATER ONTO THE ACID. A&W – Acid to water, never the other way around.) The mortars and pestles are rinsed exhaustively with water to remove all traces of acid and then scrubbed well in the sink with hot water and brushes but with no soap. They are then put into dishwasher. Thimbles are not put in the dishwasher. The equipment is rinsed 1x acetone, 4x toluene, 3x hexane, 3x DCM (all are discarded) and proceeds to the proof step.

Glass thimbles: after acid washing as described above, the thimbles are handled as little as possible, using clean tweezers and solvent-rinsed foil. The thimbles are rinsed with 6x acetone, 6x toluene, 6x hexane, and 6x DCM (all discarded) and proceed to the sediment proof step. Thimbles never go in the dishwasher and are never baked.

Soxhlets and condensers: this equipment must be handled very gently. It is rinsed 6x acetone, 6x toluene, 6x hexane, and 6x DCM (all discarded). It is easiest to rinse the condensers if they are still clamped in

place. Using a small funnel, solvent is poured down the top. The soxhlets and condensers may then proceed, as described below, to the sediment proof step. Soxhlets and condensers never go in the dishwasher and are never baked.

Centrifuge tubes: are soaked in hot water and then put into the dishwasher. The tubes are placed into a 1L beaker and then rinsed 1X with acetone. The tubes (in the beaker) are then filled with toluene and sonicated for 20 minutes. The toluene is then discarded, the tubes are refilled with toluene and sonicated again and the toluene discarded. The tubes are filled with hexane to remove the toluene and the hexane is discarded. The tubes are then put into the oven and treated as normal glassware. It is easiest to do all rinses of the tubes in a clean 1L beaker. The final DCM proof rinse is done using the Dispensette. Funnels work best for rinsing the tubes' stoppers.

Glass tips used for silica/alumina columns: are not to be dishwasher washed. They are soaked in hot water, rinsed with distilled water, and rinsed with acetone. They are then sonicated twice with toluene, discarding solvent after each sonication. The tips may then be baked as normal glassware. The tips are assembled with push-in fitting using Teflon™ tape and rinsed as described below using the Dispensette.

Push-in Teflon™ fittings: are soaked in hot water, rinsed with distilled water and, using a Pasteur Pipette, rinsed thoroughly with acetone. These, or any other, Teflon™ fittings are never put in dishwasher, sonicated or baked. Each fitting is assembled with a baked glass tip and rinsed as normal using the Dispensettes. 10 mL is considered to be three rinses. The rubber stopper should not be rinsed with solvent.

Stopcocks / Teflon™ Fittings: with the rubber washer removed, stopcocks and other Teflon™ fittings are soaked in hot water using a 1L beaker (12 to 24 Teflon™ fittings fit into a 1 L beaker). They are then rinsed with distilled water, followed by a single rinse with acetone (all rinses are discarded). The fittings are then sonicated in toluene once for 20 minutes and the solvent is discarded, followed by a rinse with hexane, which is also discarded. The Teflon™ fittings are then placed in sodium sulfate columns or separatory funnels that have been baked and rinsed as normal, this way rinsing both pieces of equipment at once. 12 stopcocks are rinsed for the GPC columns in a beaker or funnel followed by a final DCM proof rinse using the Dispensette.

Glass Wool: glass wool is rinsed thoroughly with toluene, hexane, and DCM using tongs. It is then allowed to dry in a fumehood and then wrapped with solvent-rinsed aluminum foil. Glass wool is added to sodium sulfate columns before beginning proof rinses.

Solvent-rinsed aluminum foil: is rolled and rinsed once with hexane. The rinse is discarded.

Amber micro-vials: are sonicated once in DCM once, and then sonicated in hexane once. Using tweezers, each vial is filled with solvent - this is slow but important. Solvent residues are allowed to evaporate completely from the vials in a fumehood and they are then placed in a clean container covered with solvent-rinsed foil.

Scintillation Vials: are rinsed once with hexane. Solvent residues are allowed to evaporate completely in a fumehood, and the caps are then replaced. Each flat of vials is labeled with "hexane rinsed".

Nitrogen evaporator tips: are sonicate once in toluene, and then sonicated in DCM once. Solvent residues are allowed to evaporate completely in a fumehood and the tips and placed in a clean container covered with solvent-rinsed foil.

Column solvent reservoirs: joint ends are rinsed once with 1:1 DCM:hexane after use and are then wrapped with hexane-rinsed aluminum foil and stored.

High Resolution Gas Chromatograph inlet liners: in all cleaning steps, the liners are rinsed by filling the storage tubes. The rinse is decanted by adjusting the cap to prevent the liners from falling out and then pouring the rinse out. Appropriate waste container must be used to discard dichlorodimethyl-siloxane.

1. Liners are immersed in concentrated HCl for at least 2 hrs. They are sonicated for ½ hr at the beginning AND end of this time. The HCl is then discarded.
2. Liners are rinsed with distilled H_2O, MeOH, and acetone, sonicating with each rinsing agent for 5 min. Each rinse is discarded after use.
3. Liners are dried in the oven for 2 hrs at 120°C.
4. Liners are cleaned by using a small brush or wire to dislodge any solids that may be present in the interior surface, followed by compressed N_2 to blow out any loose material.
5. Liners are immersed in dichlorodimethyl-siloxane for 24 hrs followed by sonication for ½ hr at the end of this time. The dichlorodimethyl-siloxane is then discarded into its specific waste container.
6. The storage tube is filled with MeOH and the liners are sonicated for 5 min. the MeOH is discarded.
7. Clean liners are stored in hexane.

GLASSWARE BATCHES AND PROOFS

Please read this entire section before proceeding.

The following glassware is required to collect a proof: a 1 L beaker, one small funnel, one 500 mL flask with 24/40 stopper, one 125 mL round bottom flask, two Si/Al columns, one push-in fitting, and one 15 mL centrifuge tube.

As soon as proof rinses are being collected for a glass batch, about 10 mL of DCM is put into a 500 mL round bottom flask and the flask is spiked with the appropriate surrogate internal standards for the analysis requested for that batch (see also Appendix I). The lab supervisor must be consulted regarding which spikes to use – there may be changes. The flask is labeled with the glass batch number.

Only the final DCM rinse is collected for a proof. It is easiest if these rinses are collected into a 1 L beaker. This beaker should be kept covered with hexane-rinsed foil when not in use and it should not be allowed to go dry. Once you have about 300 mL of proof rinses, the solvent from the beaker is poured into the spiked 500 mL flask, using a funnel if necessary. The proof flask contents are reduced in volume to a few mL by rotary evaporation each time the flask contains about 300 mL until the proof is complete.

The progress of each glass proof is recorded on the appropriate paper list. When the proof is completed the date is recorded on this note and then the note is taped into the student lab book. Each bundle or piece of glassware that is part of a proofed batch is labeled with its batch number. Shelves, individual pieces of glassware, and tube racks with batch numbers are also labeled clearly with the batch number.

After rotovaping the proof down to a few mL, it is put through a silica and then an alumina column (as in tissue extraction sample methodology). Glass proofs are not put through the carbon fibre step. The proof is transferred to a centrifuge tube and evaporated under nitrogen to approximately 100 µL. It is transferred to an amber vial, evaporated under nitrogen to 10-20 µL and then spiked with the appropriate surrogate recovery standards and capped.

Before spiking the proof with a surrogate recovery standard, the vial containing the standard must be at room temperature and then vortexed.

The proof vial should remain capped until just before addition of the surrogate recovery standard(s). Spiking information is recorded in laboratory log book – ALL of the information on the standard vial should be copied into the log book. Spikes are the same regardless of whether it is a tissue or sediment batch. The proof is NOT spiked with PCB 101 surrogate recovery standard.

Tissue glassware batch:

24 metal spatulas

12 weighing boats

12 porcelain mortars and pestles

12 large funnels

12 sodium sulfate columns with glass wool

24 Teflon™ fittings to fit sodium sulfate and gel permeation columns

12 500 mL round bottom flasks

12 24/40 glass stoppers

24 silica/alumina columns

12 push-in fittings and glass tips

60 125-250 mL round bottom or flat bottom round flasks

36 15 mL centrifuge tubes with stoppers

Sediment glassware batch:

There is some adjustment in composition of the glassware batch, for example, if the batch is to be analysed for ethers only, if the batch consists of blubber darts, or only if only certain PCB fractions are to be analysed.

Before doing a new glass batch proof with this glassware, the soxhlet apparatus is assembled with precleaned (prerinsed) glass thimbles and clean glass wool. 300-350 mL of 80:20 toluene:acetone are added with a few fresh boiling chips and the assembly is allowed to reflux for 4 to 6 hours. This is the pre-extraction clean up. The cooled apparatus is then dismantled and the solvent discarded.

A proof of the condensers is collected with them still in place, after the pre-extraction. The remaining part of the soxhlet apparatus (including thimbles) is then proofed along with the remainder of the glassware batch. The sediment glassware proof is spiked with the same surrogate internal and recovery standards as a tissue glassware proof.

12 soxhlet apparatus and 12 condensers
24 500 mL round bottom flasks
12 500 mL separatory funnels with stoppers to fit
12 glass thimbles with glass wool (extra coarse frit)
11 porcelain mortars and pestles
11 weighing boats
24 metal spatulas
12 large funnels
12 sodium sulfate columns
24 Teflon™ stopcocks to fit sodium sulfate columns and separatory funnels
36 silica/alumina columns
12 push-in stopcocks and glass tips
12 150 mL flat bottom round flasks
36 15 mL centrifuge tubes and stoppers
60 125-250 mL round bottom or flat bottom round flasks
glass wool for funnels

Fumehood in the glassware room:

- Waste beakers are to be emptied whenever they are not being used.
- Each night, the spouts of the solvent pour bottles should be covered with foil.

INSTRUMENTAL ANALYSIS

QA/QC PROTOCOLS AND PROCEDURES FOR THE ULTRATRACE ANALYSIS OF PCDD/F BY HRGC/HRMS

Extracted and cleaned up samples are analysed by High Resolution Gas Chromatography / High Resolution Mass Spectrometry (HRGC/HRMS) for polychlorinated dibenzodioxins / polychlorinated dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), polychlorinated diphenyl ethers (PCDEs), and pesticides. The protocols and procedures for analysis of PCDDs and PCDFs follows; the protocols and procedures for the balance of the compounds are similar and specific masses analysed for these compounds are given in Appendices VIII, IX, and X.

A. Instrumentation

1. Gas chromatography

The HRGC is a Hewlett-Packard (Palo Alto, CA) model 5890 Series II with split, splitless and on-column injection capabilities. A MS is the only on-line detector attached for all the various analyses. The GC is operated in splitless mode. The temperatures used for the splitless injector port, the direct GC/MS interface and the MS's ion source are given in Appendix VII.

The chromatographic columns used are DB™-5 (60 m x 0.25 mm i.d., 0.1 μm film thickness)(J&W Scientific (Folsom, CA)) and ultra high purity helium is used as the carrier gas at a constant head pressure of 25 psi, which maintains a linear flow velocity of 35 cm second^{-1}. The column is positioned in the injection liner at 3/4" for PCDD/F analyses and at 1 1/4" for PCB analyses. The sample volume injected is 1 μL and the splitless injector purge valve is activated 2 min after injection. The temperature programs for all of the various analyses are given in Appendix VII. All sample injections are performed via a CTC A200S autosampler (CTC Analytics, Zwingen, Switzerland). Programming and operation of both the GC and the autosampler is controlled from the MS's data system, OPUS version 2.1E (FISONS Instruments, VG Analytical, Manchester, UK).

2. Mass Spectrometry

The HRMS utilised is a VG-AutoSpec-S (FISONS Instruments, VG-Analytical, Manchester, UK). This is a sector instrument of the EBE geometry coupled to the GC via a VG-Analytical type interface. For PCDD/F analysis it is operated under positive EI conditions with the filament in the trap stabilisation mode at 600 μA and an electron energy of 28 to 35 eV. The instrument is routinely resolving at 10,000 resolution power (10K RP) and data are acquired in the Single Ion Resolving Mode

(SIR) for achieving maximum sensitivity possible. The two most abundant isotope ions, M^+ and $(M+2)^+$ in most cases, of known relative abundance are monitored for each homologue series and ^{13}C labelled surrogate standards (see Appendix II). To check for possible interferences from PCDEs corresponding ions are monitored for each homologue series. The MS experiment is divided into five time-consecutive functions. Each function is restricted to a m/z range spanning the voltage range 8 - 6 kV in order to maintain 10k RP throughout the m/z range.

All hardware and software settings, tuning, scanning and calibration of the MS are conducted in accordance with protocols established in Environment Canada report EPS 1/RM/19 (Anon., 1992), for PCDD/F analysis.

B. HRGC/HRMS

The quality assurance / quality control (QA/QC) measures undertaken for the analysis of PCDD/Fs stem from the guidelines specified by Environment Canada (Anon., 1992) and US-EPA Method 1613 (Anon., 1994). The GC/MS operating conditions are established according to the procedure described below and prior to the analysis of a batch of "real" samples.

Step 1. MS resolution

The following procedure is followed:

a. Static tuning: The MS is tuned to 10k RP spanning 8 to 6 kV with a minimum 80% transmittance using the calibrant perfluorokerosene (PFK) (m/z 293).

b. Calibration of the mass range: The mass range for each function of the MS experiment is calibrated, done by Opus™ software automatically, against a calibration file containing the specific calibrant PFK masses that occur within the function mass range (acceptable variation < 50 ppm).

c. Dynamic tuning: PFK masses within the function mass range are viewed to ensure that the resolution from lowest to highest mass remains constant (within ±1k RP).

d. Lockmass monitoring: Monitoring of one calibrant PFK mass (referred to as lockmass, Appendix II) within a function to allow continuous calibration adjustments during real-time acquisition. Any mass drifts are corrected for by maintaining the voltage differences between PFK masses that were established in the calibration file. The lockmass intensity should only vary within ±10% from the mean intensity recorded during the respective real-time acquisition, and should be <1E8 to prevent saturation of the detector and to ensure effective monitoring of any sensitivity changes that may occur during analysis.

Step 2. GC column performance

This is evaluated by injecting 1 μL of the column performance/resolution standard to confirm separation at the 25% baseline level between 1237-, 1238- and 2378-TCDDs. See Appendix III for composition and concentration of this mixture. If the specification is not met adjustments in chromatographic, interface and ion source conditions are made and the experiment is repeated until satisfactory results are obtained. This solution is run after any change in column length.

Step 3. Retention time windows

Included in the GC column performance solution is a window defining mixture (see Appendix III for composition and concentration of this mixture). Elution times of the first and last eluting isomers for tetra, penta, hexa, and hepta PCDD/Fs on a DB™-5 GC column are established from this analysis. Complete separation of at least 30 seconds is required between the last eluting isomer from the lower group to the first eluting isomer of the subsequent group. Peak widths at half height should be between 4 and 6 seconds for all congeners.

This is a QC measure and is needed to adjust the column carrier gas head pressure such that the homologues elute within the defined retention time windows for selected ion monitoring (SIM). This experiment is performed after any change in column length.

If this specification is not met the chromatographic conditions are adjusted and steps 1 and 2 are repeated.

Step 4. Ultimate sensitivity, signal-to-noise ratio (S/N)

1 μL of a 100 fg μL^{-1} solution of each of 2,3,7,8-TCDD and the corresponding surrogate is used. The response recorded for m/z 321.8936 of 2,3,7,8-TCDD should be at least 10 times higher than the background noise, a noise height at two standard deviations is considered.

If this specification is not met, re-tune the instrument and/or adjust chromatographic and interface conditions in which case satisfactory data for all the previous steps would need to be reconfirmed. This analysis is repeated daily with each batch of samples analysed.

Step 5. Multipoint calibration and linearity

This QC measure is required to check the linearity of the MS's response for the five calibration solutions (standards CS1 to CS5, compositions and concentrations listed in Appendix IV). The relative response factors (RRF) for all surrogate and native PCDD/Fs are computed at each concentration with respect to a surrogate recovery standard and surrogate internal standard, respectively (see Appendix V for sample

calculations). The coefficients of variation of the RRFs over the five-point calibration range must be less than 20% in order to demonstrate linearity. Once this criterion is met then the average RRF of CS1 to CS5 for that congener may be used for quantification.

Corrective action is necessary if linearity is not demonstrated. Following those corrections, re-injection of solutions CS1 to CS5 would be required.

Analysis of the CS1 to CS5 is performed only if the results from continuous calibration verification runs (step 9) are outside the acceptable limits.

Step 6. Instrument Detection limits

Responses of all isomers established from the analysis of the CS1 solution, apart from being used to compute RRFs, are also used to establish the instruments detection limits for each of the isomers, see Appendix V-D. This detection limit evaluation is complementary to that of step 4.

Step 7. Sample carryover

Sample carryover is assessed by analysing solvent blanks. An injection of toluene is made after the CS3 solution to verify that there is minimum carryover of analytes, i.e. to check on whether there are any residues in the system, including the injector, an etched syringe, GC column, GC/MS interface, and ion source. The intensities/response of all native compounds should be less than 0.4% from those obtained from the analysis of the CS3 solution.

If carryover is high there is a need to determine areas where the sample is aggregating. Step 7 is repeated. If major changes are made some or all of the above steps need to be repeated.

Step 8. Analysis of a batch of "real" samples

Every batch consists of a total of 9 samples and those samples may include:
1 procedural/method blank. A QA/QC provision to check the cleanliness of the extraction and clean up method is. This step can also be considered as QA/QC for the glassware.
1 duplicate. A repeat analysis is conducted for one of the 9 samples (not the blank or reference material) randomly selected. QA/QC measures are applied to demonstrate instrumental precision.
1 certified or other reference material sample. Also a QA/QC provision to check the accuracy of the data. This involves a fortified fish sample spiked with Environment Canada or US-EPA certified solutions of PCDD/F. This sample ideally should be a certified reference material (CRM).

If recoveries of surrogates in any of the samples are outside the acceptable 30 to 120% range, the sample may be re-extracted and re-analysed.

All samples analysed, regardless whether each set includes any or all of the samples listed above, are ranked such that instances of high concentration samples preceding low concentration samples are minimised. Ranking information is acquired based on sample type, sampling location, and sample age.

Step 9. Closing continuous calibration verification.

At the end of the analysis of the samples in step 7, the CS3 calibration solution is re-analysed to verify instrument stability over the period required to execute steps 5 and 8. This is established by comparing the RRFs computed from the results of this experiment against the average RRFs computed in step 5, the acceptable drift limits are outlined below. Prior to starting analysis of another batch of real samples, steps 1 and 4 are repeated. The CS1 solution is analysed to confirm instrumental detection limits for all isomers. Analysis of the CS1 solution is followed by step 9.

Step 10. Continuing calibration verification

Calibration is continually verified by analysing a CS3 standard solution before and after every 10 "real" samples. The RRFs established from analysis of this solution, for 2,3,7,8-TCDF and 2,3,7,8-TCDD, must be within 15% of those obtained in step 5. The calculated RRFs of all other analytes must be within 20% of the corresponding RRF values in step 5 and within 25% for each of the surrogate compounds. This QC measure checks on whether linearity over the dynamic range, defined by the concentrations of the solutions CS1 to CS5, is still in effect.

If response factors are outside the allowable limits, the CS3 solution is re-injected after re-tuning the MS (step 1). If response factors are still out of range then step 5 is repeated, i.e. re-calibration is required.

Once the results of this experiment are satisfactory, it is followed by analysis of CS3 followed by a solvent blank sample (step 7) and then by another 10 "real" samples. Thereafter, more calibrant gas is added and the cycle is repeated (see also Appendix VI).

C. Data presentation

The ions monitored for all calibration and real sample experiments are listed in Appendix II. Raw data ion chromatograms are processed using identical smoothing, background subtraction, normalisation and peak integration parameters for both calibration and real sample data and are hard copies are made. Since the data are normalised to the most intense peak, isomers of low intensity relative to others will appear as background peaks. In this case the data is using the same parameters but with a specified lower intensity such that the minor components in the chromatogram may be quantified.

MS-processed data undergo preliminary data QA and electronic processing (see Appendix XI), followed by QA/QC evaluation (see Appendices XIII, XIV, XV) and are quantified using the average RRFs for each compound obtained from the analysis of the calibration solutions. In the final report all data related to the analysis are presented including: sample weight/volume, concentrations of native compounds, amounts of surrogates added, calculated limits of detection (MDL), percent surrogate recoveries, percent lipid or moisture, and sampling site. An assigned laboratory number identifies the samples. Examples of final reports are given in Appendix XII.

D. Qualitative determination. Criteria for Positive Identification.

(Criteria for analyte identification are also specified in both EPS (section 6.5) and EPA 1613 methods)

Compounds are identified as PCDD/F (either native or surrogate), only when the chromatographic peaks obtained from the HRGC/HRMS analysis satisfy all of the following criteria:

1. Two isotopes of the specific congeners are detected at their exact m/z (Appendix II) at a minimum 10k RP during the entire chromatographic run.

2. Both of the isotope signals in criterion 1. must be present, and must maximise within $\pm$ 2 seconds of one another.

3. The retention time of a specific congener must be within 3 seconds to that obtained during analysis of the authentic compounds in the calibration standards. In the case of a congener for which a labelled analogue is present in the surrogate spiking solution, all native and surrogate ion peak maxima must be coincident within 3 seconds.

4. The signal-to-noise ratio of each of the isotope m/z channels must be ≥ 3 for a sample extract, and ≥ 10 for a calibration standard.

5. The ratio between the integrated isotope signals of each congener must be within the limits outlined in Appendix II.

6. The elution times of all native PCDD/Fs, must be within the retention time windows established in section I, step 3.

7. Confirmatory analysis is required for 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TeCDF) if its concentration exceeds 50 pg g^{-1}. On a 60m DB™-5 column, 2,3,7,8-TeCDF cannot be resolved from its neighbouring isomers. A 30m DB™-225 is used to resolve 2,3,7,8-TeCDF from its neighbouring 2,3,4,7- and 1,2,3,9-TeCDF isomers. The operating conditions are adjusted accordingly for analysis on the second GC column. The GC/MS must meet the mass resolution and calibration specifications outlined in section I.

Once the identification criteria are met, compounds are quantified by the isotope dilution method.

E. Quantitative determination.

The isotope dilution method is used to quantify PCDD/Fs using surrogates for internal and recovery standards. By adding a known amount of a surrogate compound to every sample prior to extraction, correction for recovery of the native compound can be made because the native compound and its surrogate analogue will be affected similarly during sample preparation and HRGC/HRMS analysis. The method is based on the use of RRFs, see Appendix V-A,B,C. For the native standards, the RRF is the ratio between the response factors (RFs) of the analyte and of the corresponding surrogate internal standard. For the surrogate internal standards, the RRF is the ratio between the RF of the surrogate internal standard and the corresponding surrogate recovery standard. These RRFs are constant over the concentration range for which MS response is linear. Using mean RRFs determined from the calibration standards CS1 to CS5, along with native and surrogate responses from the samples, recovery corrected concentrations of PCDD/Fs are calculated.

This quantification method relies upon consistent linearity of MS response over time and over the concentration range represented by the standard solutions of Appendix IV. The method is integrated into an automated routine for data quantification.

In general, the criteria for identification and quantification and the quality control measures undertaken for the analysis of all analytes indicated above were based on protocols established in Environment Canada report EPS 1/RM/19, February 1992, for polychlorinated dibenzo-p-dioxin and furan analysis.

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APPENDIX I

Surrogate Internal Standard Spiking Amounts*

Analysis	Congener	Amount spiked (pg)
PCDD/Fs	$^{13}C_{12}$-2,3,7,8-Tetrachlorodibenzo-p-dioxin	995
	$^{13}C_{12}$-1,2,3,7,8-Pentachlorodibenzo-p-dioxin	995
	$^{13}C_{12}$-1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin	995
	$^{13}C_{12}$-1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin	995
	$^{13}C_{12}$-Octachlorodibenzo-p-dioxin	1990
	$^{13}C_{12}$-2,3,7,8-Tetrachlorodibenzofuran	995
	$^{13}C_{12}$-1,2,3,7,8-Pentachlorodibenzofuran	995
	$^{13}C_{12}$-1,2,3,4,7,8-Hexachlorodibenzofuran	995
	$^{13}C_{12}$-1,2,3,4,6,7,8-Heptachlorodibenzofuran	995
DO[A]- PCBs	$^{13}C_{12}$-2,2',5,5'-tetrachlorobiphenyl (PCB 52)	1896
	$^{13}C_{12}$-2,2',4,5,5'-pentachlorobiphenyl (PCB 101)	2004
	$^{13}C_{12}$-2,2',3,3',4,4'-hexachlorobiphenyl (PCB 128)	1897
	$^{13}C_{12}$-2,2',3,4,4',5,5'-heptachlorobiphenyl (PCB 180)	1882
	$^{13}C_{12}$-2,2',3,3',4,4',5,5'-octachlorobiphenyl (PCB 194)	1979
	$^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl (PCB 208)	1939
	$^{13}C_{12}$-2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl (PCB 209)	2185
MO[B]-PCBs	$^{13}C_{12}$-2,4,4'-trichlorobiphenyl (PCB 28)	1093
	$^{13}C_{12}$-2,3',4,4',5-pentachlorobiphenyl (PCB 118)	957
	$^{13}C_{12}$-2,3,3',4,4'-pentachlorobiphenyl (PCB 105)	1022
	$^{13}C_{12}$-2,3,3',4,4',5-hexachlorobiphenyl (PCB 156)	988
NO[C]-PCBs	$^{13}C_{12}$-4,4'-dichlorobiphenyl (PCB 15)	984
	D5-3,4,5-trichlorobiphenyl (PCB 38)	951
	$^{13}C_{12}$-3,3',4,4'-tetrachlorobiphenyl (PCB 77)	840
	$^{13}C_{12}$-3,3',4,4',5-pentachlorobiphenyl (PCB 126)	977
	$^{13}C_{12}$-3,3',4,4',5,5'-pentachlorobiphenyl (PCB 169)	970
PCDEs	$^{13}C_{12}$-3,3',4,4'-tetrachlorodiphenyl ether (CDPE 77)	1000
	$^{13}C_{12}$-2,2',3',4,4'-pentachlorodiphenyl ether (CDPE 105)	1000
	$^{13}C_{12}$-2,3,3',4,4',5-hexachlorodiphenyl ether (CDPE 156)	2000

	$^{13}C_{12}$-2,2',3,3',4,4',5-heptachlorodiphenyl ether (CDPE 170)	2000
	$^{13}C_{12}$-2,2',3,3',4,4',5,5'-octachlorodiphenyl ether(CDPE 194)	3000
PBDEs	$^{13}C_{12}$-2,4,4'-tribromodiphenyl ether (BDE 28)	3260
	$^{13}C_{12}$-2,2',4,4'-tetrabromodiphenyl ether (BDE 47)	2500
	$^{13}C_{12}$-2,2',4,4',5-pentabromodiphenyl ether (BDE 99)	3750
	$^{13}C_{12}$-2,2',4,4',6-pentabromodiphenyl ether (BDE 100)	3750
	$^{13}C_{12}$-3,3',4,4',5-pentabromodiphenyl ether (BDE 126)	3750
	$^{13}C_{12}$-2,2',4,4',5,6'-hexabromodiphenyl ether (BDE 154)	3260
	$^{13}C_{12}$-2,2',3,4,4',5',6-heptabromodiphenyl ether (BDE 183)	3260
	$^{13}C_{12}$-2,2',3,3',4,4',5,5',6,6'-decabromodiphenyl ether (BDE 209)	12360
Pesticides	$^{13}C_6$-chlorobenzene	2972
	$^{13}C_6$-1,4-dichlorobenzene	2972
	$^{13}C_6$-1,2,3-trichlorobenzene	2972
	$^{13}C_6$-1,2,3,4-tetrachlorobenzene	2972
	$^{13}C_6$-pentachlorobenzene	2972
	$^{13}C_6$-hexachlorobenzene	2972
	$^{13}C_8$-Mirex	2304
	$^{13}C_6$-Lindane	3140
	$^{13}C_{12}$-p,p'-DDE	3004
	$^{13}C_{12}$-p,p'-DDT	3248
	D_4-alpha-endosulfan	19760
	$^{13}C_{12}$-2,2',4,5,5'-pentachlorobiphenyl (PCB-101)	2936

Surrogate Recovery Standard Spiking Amounts*

Analysis	Congener	Amount spiked (pg)
PCDD/Fs	$^{13}C_{12}$-1,2,3,4-Tetrachlorodibenzo-p-dioxin	1000
	$^{13}C_{12}$-1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin	1000
Diortho PCBs and Pesticides	$^{13}C_{12}$-2,3,3',5,5'-pentachlorobiphenyl (PCB 111)	2008
MO-PCBs[B], NO-PCBs[C]	$^{13}C_{12}$-2,2',4,5,5'-pentachlorobiphenyl (PCB-101)	1008
PCDEs	$^{13}C_{12}$-2,2',3,3',4,4'-hexachlorodiphenyl ether (CDE 128)	1000
PBDEs	$^{13}C_{12}$-3,3',4,4'-tetrabromodiphenyl ether (BDE 77)	1000

*All ^{13}C labelled and deuterated standards purchased from Cambridge Isotope Laboratories, Andover, MA, U.S.A. except for the pesticide surrogate internal standards, which were purchased as a cocktail from Axys Analytical Ltd., Sidney, B.C.

[A] di/tri/tetra-substituted

[B] mono-ortho-substituted

[C] non-ortho-substituted

APPENDIX II

PCDD/F Masses (SIR), Ion Type and Isotope Ratio Control Limits

Compound	Quantification Ions (m/z) 1st	2nd	Ion Type	Isotope Ratio
TeCDF	303.9016	305.8987	M/M+2	0.65 - 0.89
$^{13}C_{12}$-TeCDF	315.9419	317.9389	M/M+2	0.65 - 0.89
TeCDD	319.8965	321.8936	M/M+2	0.65 - 0.89
$^{13}C_{12}$-TeCDD	331.9368	333.9339	M/M+2	0.65 - 0.89
HxCDPE[a]	375.8364		M+2	
PFK	316.9824		Lock	
PeCDF	339.8597	341.8568	M+2/M+4	1.32 - 1.78
$^{13}C_{12}$-PeCDF	351.9000	353.8970	M+2/M+4	1.32 - 1.78
PeCDD	353.8576	355.8546	M/M+2	0.53 - 0.71
$^{13}C_{12}$-PeCDD	365.8978	367.8949	M/M+2	0.53 - 0.71
HpCDPE[a]	409.7974		M+2	
PFK	366.9792		Lock	
HxCDF	373.8207	375.8178	M+2/M+4	1.05 - 1.43
$^{13}C_{12}$-HxCDF	383.8639	385.8610	M/M+2	0.43 - 0.59
HxCDD	389.8156	391.8127	M+2/M+4	1.05 - 1.43
$^{13}C_{12}$-HxCDD	401.8559	403.8530	M+2/M+4	1.05 - 1.43
OcCDPE[a]	445.7555		M+4	
PFK	380.9760		Lock	
HpCDF	407.7818	409.7788	M+2/M+4	0.88 - 1.20
$^{13}C_{12}$-HpCDF	417.8253	419.8220	M/M+2	0.37 - 0.51
HpCDD	423.7767	425.7737	M+2/M+4	0.88 - 1.20
$^{13}C_{12}$-HpCDD	435.8169	437.8140	M+2/M+4	0.88 - 1.20
NoCDPE[a]	479.7165		M+4	
PFK	430.9728		Lock	
OCDF	441.7428	443.7398	M+2/M+4	0.76 - 1.02
OCDD	457.7377	459.7348	M+2/M+4	0.76 - 1.02
$^{13}C_{12}$-OCDD	469.7780	471.7750	M+2/M+4	0.76 - 1.02
DeCDPE[a]	513.6775		M+4	

PFK	454.9728	Lock

Notes:

1. Molecular ions of PCDEs have the same m/z and isotope ratio as the PCDFs (at a chlorination level of 2 less Cl than the PCDE) so quantification of PeCDFs must be adjusted according to the measured PCDE responses. Any PeCDF with a co-eluting PCDE of ≥5% area response of the total PeCDF response must be considered not detectable.
2. Both the native and surrogate PeCDD M+4 ion have interference at 10k RP from one, therefore the less intense M^+ is monitored instead.

APPENDIX III

GC Column Performance Standard / Window Defining Solution

GC Column Performance Standard (ED-908C, Cambridge Isotope Laboratories, Andover, MA, U.S.A.)

Isomer	Concentration (pg μL^{-1})
1,2,3,4-TeCDD	10
1,2,3,7/1,2,3,8-TeCDD	10
1,2,6,7-TeCDD	20
1,2,7,8-TeCDD	20
1,4,7,8-TeCDD	10
2,3,7,8-TeCDD	10

Window defining solution (EF-1731A plus ED-1732A, Cambridge Isotope Laboratories, Andover, MA, U.S.A.)

First and last eluting tetra to hepta dioxin and furan isomers on DB™-5 type GC columns. All isomers at 10 pg μL^{-1}.

First eluting isomer	Last eluting isomer
1,3,6,8-TeCDD	1,2,8,9-TeCDD
1,3,6,8-TeCDF	1,2,8,9-TeCDF
1,2,4,6,8/1,2,4,7,9-PeCDD	1,2,3,8,9-PeCDD
1,3,4,6,8-PeCDF	1,2,3,8,9-PeCDF
1,2,4,6,7,9/1,2,4,6,8,9-HxCDD	1,2,3,4,6,7-HxCDD
1,2,3,4,6,8-HxCDF	1,2,3,4,8,9-HxCDF
1,2,3,4,6,7,9-HpCDD	1,2,3,4,6,7,8-HpCDD
1,2,3,4,6,7,8-HpCDF	1,2,3,4,7,8,9-HpCDF

APPENDIX IV

Calibration Solutions: Concentrations of CS1 to CS5 (pg μL^{-1})[a]

Native PCDDs and PCDFs	CS1[b]	CS2	CS3[c]	CS4	CS5
2,3,7,8-TeCDD	0.25	1	5	20	100
2,3,7,8-TeCDF	0.25	1	5	20	100
1,2,3,7,8-PeCDD	1.25	5	25	100	500
1,2,3,7,8-PeCDF	1.25	5	25	100	500
2,3,4,7,8-PeCDF	1.25	5	25	100	500
1,2,3,4,7,8-HxCDD	1.25	5	25	100	500
1,2,3,6,7,8-HxCDD	1.25	5	25	100	500
1,2,3,7,8,9-HxCDD	1.25	5	25	100	500
1,2,3,4,7,8-HxCDF	1.25	5	25	100	500
1,2,3,6,7,8-HxCDF	1.25	5	25	100	500
1,2,3,7,8,9-HxCDF	1.25	5	25	100	500
2,3,4,6,7,8-HxCDF	1.25	5	25	100	500
1,2,3,4,6,7,8-HpCDD	1.25	5	25	100	500
1,2,3,4,6,7,8-HpCDF	1.25	5	25	100	500
1,2,3,4,7,8,9-HpCDF	1.25	5	25	100	500
OCDD	2.5	10	50	200	1000
OCDF	2.5	10	50	200	1000
Labelled PCDD/Fs					
$^{13}C_{12}$-1,2,3,4-TeCDD[d]	50	50	50	50	50
$^{13}C_{12}$-2,3,7,8-TeCDD[f]	50	50	50	50	50
$^{37}Cl_4$-2,3,7,8-TeCDD[g]	0.25	1	5	20	100
$^{13}C_{12}$-2,3,7,8-TeCDF[f]	50	50	50	50	50
$^{13}C_{12}$-1,2,3,7,8-PeCDD[f]	50	50	50	50	50
$^{13}C_{12}$-1,2,3,7,8-PeCDF[f]	50	50	50	50	50
$^{13}C_{12}$-2,3,4,7,8-PeCDF[g]	50	50	50	50	50
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD[g]	50	50	50	50	50
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD[f]	50	50	50	50	50
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD[e]	50	50	50	50	50
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF[f]	50	50	50	50	50
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF[g]	50	50	50	50	50
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF[g]	50	50	50	50	50

$^{13}C_{12}$-2,3,4,6,7,8-HxCDF[g]	50	50	50	50	50
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD[f]	50	50	50	50	50
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF[f]	50	50	50	50	50
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF[g]	50	50	50	50	50
$^{13}C_{12}$-OCDD[f]	100	100	100	100	100

[a]Calibration solutions CS1 to CS5 were purchased from Cambridge Isotope Laboratories (Andover, MA, U.S.A) at double the concentrations indicated in the table, dilutions with toluene were performed in-house

[b]also used to verify detection limits

[c]used to verify RRF stability with respect to initial calibration, analysed daily before and after the analysis of a batch of 10 real samples

[d] surrogate recovery standard for tetra and penta-CDD/F

[e]retention time marker and surrogate recovery standard for hexa and hepta-CDD/F and OCDD

[f]labeled PCDDs and PCDFs used as surrogate internal standards in the extraction and cleanup procedure

[g]present in the calibration solutions purchased from CIL but not used for quantification.

APPENDIX V

Sample calculation of relative response factors (RRFs)

The example given is the RRF determination of 2,3,7,8-TeCDD with respect to ^{13}C-2,3,7,8-TeCDD. Areas used are the sum of the isotopic peak areas. Analyte and surrogate concentrations are in pg μL^{-1}.

$$RRF = \frac{\text{Area of 2,3,7,8-TeCDD}}{\text{Area of } ^{13}\text{C-2,3,7,8-TeCDD}} \times \frac{[^{13}\text{C-2,3,7,8-TeCDD}]}{[\text{2,3,7,8-TeCDD}]}$$

The mean RRF is calculated from the five calibration solution runs where the concentration of ^{13}C-2,3,7,8-TeCDD is kept constant while the concentration of 2,3,7,8-TeCDD is increased from 0.25 to 100 pg, see Appendix IV.

Sample calculation of percent recovery of surrogate internal standard ^{13}C-2,3,7,8-TeCDD

The surrogate recovery standards are added just before HRGC/HRMS analysis in order to determine surrogate internal standard losses during sample preparation. Percent recoveries of surrogate internal standards are calculated using RRFs with respect to a surrogate recovery standard, either $^{13}C_{12}$-1,2,3,4-TeCDD or $^{13}C_{12}$-1,2,3,7,8,9-HxCDD. As indicated in Appendix IV, $^{13}C_{12}$-1,2,3,4-TeCDD is the surrogate recovery standard for tetra and penta-CDD/F, and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD is the surrogate recovery standard for hexa and hepta-CDD/F and OCDD. Surrogate internal and recovery standard concentrations are in pg. The RRF used is for 2,3,7,8-TeCDD relative to 13C-2,3,7,8-TeCDD.

$$\%\ \text{recovery}\ ^{13}\text{C-2,3,7,8-TeCDD} = \frac{\text{Area of } ^{13}\text{C-2,3,7,8-TeCDD}}{\text{Area of } ^{13}\text{C-1,2,3,4-TeCDD}} \times \frac{^{13}\text{C-1,2,3,4-TeCDD (pg)}}{\text{RRF} \times\ ^{13}\text{C-2,3,7,8-TeCDD}} \times 100\%$$

Sample calculation of the analyte concentration

The example given is the determination of [2,3,7,8-TeCDD] in an unknown sample using the isotope dilution approach with ^{13}C-2,3,7,8-TeCDD as the surrogate

internal standard against which RRFs have been established. Analyte and surrogate concentrations are in pg and pg μL^{-1}, respectively. The product of this equation is the concentration of native analyte in the original sample before any processing began.

$$[2,3,7,8\text{-TeCDD}] = \frac{\text{Area of 2,3,7,8-TeCDD}}{\text{Area of } ^{13}\text{C-2,3,7,8-TeCDD}} \times \frac{^{13}\text{C-2,3,7,8-TeCDD (pg)}}{\text{mean RRF x sample weight (g)}}$$

Sample calculation of the method detection limit (MDL)

The example given is to the calculation of a homologue MDL with ^{13}C-2,3,7,8-TeCDD as its surrogate internal standard. MDLs are reported for each homologue series on a sample specific basis and are calculated as the concentration corresponding to the area rejected. The calculation involves three steps: a) measurement of the height of the background noise, b) calculation of the minimum detectable area (based upon three times the maximum height of the noise), and c) calculation of the homologue MDL against the concentration and peak area of ^{13}C-2,3,7,8-TeCDD. Only peaks with responses greater than three times the background noise level are quantified. The mean RRF used corresponds to the mean of the determined RRFs for a homologue series.

$$\text{Noise height (ion counts)} = \frac{\text{Noise height (mm)}}{\text{full scale height (mm)}} \times \text{full scale intensity (ion counts)}$$

$$\text{Minimum Detectable Area} = \text{noise height} \times \frac{^{13}\text{C-2,3,7,8-TeCDD Area}}{^{13}\text{C-2,3,7,8-TeCDD Height}} \times 3$$

$$\text{MDL for 2,3,7,8-TeCDD} = \frac{\text{Minimum Detectable Area}}{\text{Area of } ^{13}\text{C-2,3,7,8-TeCDD}} \times \frac{[^{13}\text{C-2,3,7,8-TeCDD}]}{\text{mean RRF x sample weight (g)}}$$

These sets of equation simplify and may be generalised to yield:

$$\text{MDL in pg g}^{-1} = \frac{\text{noise height (intensity) X 3}}{\text{Surrogate internal standard peak height (intensity)}} \times \frac{\text{amount of surrogate in vial (pg)}}{\text{RRF X weight of sample (g)}}$$

APPENDIX VI

Typical sample batch composition for PCDD/PCDF analysis on the HRGC/HRMS

Day 1.

2. Continuous calibration check, analysis of CS3 solution.
3. Instrument sensitivity check, 100 fg 2378-TCDD injection
4. Column resolution (ED-908C) and window solution (EF1731-A/ ED1732-A) (see Appendix III, combined solution
5. GC carry-over check, injection of toluene
6. Analysis of 10 real samples.
7. Continuous calibration check, analysis of CS3 solution.
8. GC carry-over check, injection of toluene
9. Analysis of 10 real samples.
10. Continuous calibration check, analysis of CS3 solution.

Day 2.

1. Continuous calibration check, analysis of CS3 solution.
2. Instrument sensitivity check, 100 fg 2378-TCDD injection
3. Analysis of 10 real samples.
4. Continuous calibration check, analysis of CS3 solution.
5. GC carry-over check, injection of toluene
6. Analysis of 10 real samples.
7. Continuous calibration check, analysis of CS3 solution.

The batch composition of Day 3 and onwards is the same as that of Day 2.

Every three months the NIST 1614 (National Institute of Standards and Technology Standard Reference Material 1614: 2,3,7,8-TCDD in isooctane) solution is analysed. Every 24 samples one of the samples is analysed in duplicate on the HRGC/HRMS.

APPENDIX VII

Gas Chromatographic Parameters

Parameter	Type of Analysis						
	PCDD/F	MO-PCB or CP-PCB	DO-PCB	BDE	CDE	PESTICIDE F1/F2 fraction	PESTICIDE F3 fraction
Run time (minutes)	53.3	44.5	50.3	56	50.5	41.3	30.3
Temperature #1 (°C)	100	80	80	100	100	80	80
Time #1 (minutes)	2	2	2	1	1	3	3
Rate #1 (°C/minute)	20	8	8	2	4	15	15
Temperature #2 (°C)	200	150	150	140	290	160	190
Time #2 (minutes)	0	0	0	0	2	0	0
Rate #2 (°C/minute)	1	4	4	4	0	5	4
Temperature #3 (°C)	215	285	300	220	0	300	270
Time #3 (minutes)	7	0	2	0	0	5	0
Rate #3 (°C/minute)	4	0	0	8	0	0	0
Temperature #4	300	0	0	330	0	0	0
Time #4 (minutes)	3	0	0	1.2	0	0	0
Injector B temperature (°C)	282	282	282	300	282	250	225
Purge B start (minutes)	2	2	2	2	1	0.50	2
Mass spectrometer source temperature (°C)	305	305	305	315	305	300	300
Interface line temperature (°C)	270	260	260	275	260	250	250

APPENDIX VIII

PCB M/Z (SIR), Ion Type and Isotope Ratio Control Limits

A. Di/tri/tetra-ortho substituted PCBs (Fraction I)

Compound	Quantification Ions (m/z) 1st	2nd	Ion Type	Isotope Ratio	PCBs Monitored
DiCB	222.0003	223.9975	M/M+2	1.23-1.85	4/10
TrCB	255.9613	257.9585	M/M+2	0.82-1.24	19,30,18,17,27/24,16/32
$^{13}C_{12}$-TrCB	268.0020	269.9990	M/M+2	0.88-1.20	^{13}C-PCB 28
TeCB	289.9224	291.9195	M/M+2	0.62-0.92	54,50,53,51,45,46,69,73/52,43,49,47/75/48,65,62, 44,59/42,71/41/64,40
$^{13}C_{12}$-TeCB	301.9626	303.9597	M/M+2	0.60-0.90	^{13}C-PCB 52
PeCB	325.8805	327.8776	M+2/M+4	1.24-1.86	104,96,103,100,94,98,102/93,95,88,121,91,92/84, 89,101/90,113,99,119,112, 109/83,97/86 116/125/117,115/87,85,110,82
$^{13}C_{12}$-PeCB	337.9207	339.9177	M+2/M+4	1.33-1.87	^{13}C-PCB 101, ^{13}C-PCB 111
HxCB	359.8415	361.8385	M/M+2	0.99-1.49	155,150,152,145,148,136,154,151,135/144,147, 149,139/140,143/134,142/131, 133,165,146/161,132/153,168,141,137,130,160/163 /164/138,158,129,166,128
$^{13}C_{12}$-HxCB	371.8817	373.8788	M/M+2	1.06-1.44	^{13}C-PCB 128
HpCB	393.8025	395.7996	M/M+2	0.83-1.25	188,184,179,176,186,178,175,187/182,183,185,174 /181,177,171,173,192/172,180,193,191,170/190
$^{13}C_{12}$-HpCB	405.8430	407.8400	M+2/M+4	0.88-1.20	^{13}C-PCB 180
OcCB	427.7640	429.7610	M+2/M+4	0.71-1.07	202,200,204,197,199,198,201,203/196,195,194,205
$^{13}C_{12}$-OcCB	439.8040	441.8010	M+2/M+4	0.76-1.02	^{13}C-PCB 194
NoCB	461.7250	463.7220	M+2/M+4	0.62-0.94	208,207,206
$^{13}C_{12}$-NoCB	473.7650	475.7620	M+2/M+4	0.66-0.90	^{13}C-PCB 208
DeCB	497.6830	499.6800	M+4/M+6	0.94-1.40	209
$^{13}C_{12}$-DeCB	509.7230	511.7200	M+4/M+6	0.99-1.35	^{13}C-PCB 209
[illegible]					

B. Mono-ortho substituted PCBs (Fraction II)

Compound	Quantification Ions (m/z) 1st	2nd	Ion Type	Isotope Ratio	PCBs Monitored
DiCB	222.0003	223.9975	M/M+2	1.23-1.85	7/9,6,8/5
TrCB	255.9613	257.9585	M/M+2	0.82-1.24	23,34,29,26,25,31,28,21,33/20,22
$^{13}C_{12}$-TrCB	268.0020	269.9990	M/M+2	0.88-1.20	^{13}C-PCB 28
TeCB	289.9224	291.9195	M/M+2	0.62-0.92	72,68,57,67,58,63,61/74,70/76,66,55,56/60
PeCB	325.8805	327.8776	M+2/M+4	1.24-1.86	101,111,120,124,108/107,123,118/106,114,122,105
$^{13}C_{12}$-PeCB	337.9207	339.9177	M+2/M+4	1.33-1.79	^{13}C-PCB 101, ^{13}C-PCB 118, ^{13}C-PCB 105
HxCB	361.8385	363.8356	M+2/M+4	0.99-1.49	159,162,167,156,157
$^{13}C_{12}$-HxCB	373.8788	375.8758	M+2/M+4	1.99-2.69	^{13}C-PCB 156
HpCB	395.7996	397.7967	M+2/M+4	1.48-2.22	189
[illegible]					

C. Non-ortho substituted (coplanar) PCBs (Fraction III/IV)

Compound	Quantification Ions (m/z) 1st	2nd	Ion Type	Isotope Ratio	PCBs Monitored
DiCB	222.0003	223.9975	M/M+2	1.23-1.85	14,11,12,13,15
$^{13}C_{12}$-DiCB	234.0410	236.0380	M/M+2	1.31-1.77	^{13}C-PCB 15
TrCB	255.9613	257.9585	M/M+2	0.82-1.24	36,39,38,35,37
D_5-TrCB	260.9928	262.9899	M/M+2	0.88-1.20	D_5-PCB 38
TeCB	289.9224	291.9195	M/M+2	0.62-0.92	80,101,79,78,81,77
$^{13}C_{12}$-TeCB	301.9626	303.9597	M/M+2	0.60-0.90	^{13}C-PCB 77
PeCB	325.8805	327.8776	M+2/M+4	1.24-1.86	127,126
$^{13}C_{12}$-PeCB	337.9207	339.9177	M+2/M+4	1.33-1.87	^{13}C-PCB 126
HxCB	361.8385	363.8356	M/M+2	1.87-2.81	169
$^{13}C_{12}$-HxCB	373.8788	375.8758	M+2/M+4	1.99-2.69	^{13}C-PCB 169

PeCDD*	353.8576		Monitored but not used in quantification
HpCB	395.7996	397.7967	Monitored but not used in quantification
[redacted]			

*PeCDD and HxCB both have mass fragments at m/z 361.8385 and 363.8356 and PCB 169 elutes on DB™-5 very close to a PeCDD. The RDL, in the past, monitored PeCDD during analysis of PCB 169 to mathematically correct any contribution (usually < 5%) this co-eluting PeCDD made to PCB 169. PCB 169 is now resolved in time from this PeCDD so the correction is no longer required.

APPENDIX IX

Diphenyl Ether Masses (SIR), Ion Type and Isotope Ratio Control Limits

A. Brominated Diphenyl Ethers (BDE)

Compound	Quantification Ions (m/z)		Ion Type	Isotope Ratio	Diphenyl Ethers Monitored
	1st	2nd			
MoBDE	247.9837	249.9817	M/M+2	0.82-1.22	1,2,3
DiBDE	325.8942	327.8922	M/M+2	0.41-0.61	10,7,8/11,12,13,15
TriBDE	245.9680	247.9661	M-Br_2/(M+2)-Br_2	0.82-1.22	30,32,17,25,28/33,35,37
$^{13}C_{12}$-TriBDE	258.0083	260.0063	M-Br_2/(M+2)-Br_2	0.88-1.18	^{13}C-BDE-28
TeBDE	323.8785	325.8765	M-Br_2/(M+2)-Br_2	0.41-0.61	75,49,71,47,66
TeBDE	483.7132	485.7112	M+2/M+4	0.58-0.78	77
$^{13}C_{12}$-TeBDE	335.9188	337.9168	M-Br_2/(M+2)-Br_2	0.43-0.59	^{13}C-BDE 47
$^{13}C_{12}$-TeBDE	495.7534	497.7514	M+2/M+4	0.58-0.78	^{13}C-BDE 77
PeBDE	403.7870	405.7850	(M+2)-Br_2/(M+4)-Br_2	0.82-1.22	100,119,99,116,85,126,105
$^{13}C_{12}$-PeBDE	415.8273	417.8252	(M+2)-Br_2/(M+4)-Br_2	0.88-1.18	^{13}C-BDE-100,99,126
HxBDE	481.6975	483.6955	(M+2)-Br_2/(M+4)-Br_2	0.54-0.82	155,154,153,140,138/166
$^{13}C_{12}$-HxBDE	493.7378	495.7357	(M+2)-Br_2/(M+4)-Br_2	0.58-0.78	^{13}C-BDE 156
HpBDE	561.6060	563.6040	(M+4)-Br_2/(M+6)-Br_2	0.82-1.22	183, Hp III, Hp IV, 181,190
$^{13}C_{12}$-HpBDE	573.6462	575.6442	(M+4)-Br_2/(M+6)-Br_2	0.88-1.18	^{13}C-BDE-183
OcBDE	639.5156	641.5145	(M+4)-Br_2/(M+6)-Br_2	0.62-0.92	Oc I, Oc II, Oc III, Oc IV
NoBDE	719.4250	721.4230	(M+4)-Br_2/(M+6)-Br_2	0.82-1.22	208,207,206
DeBDE	797.3355	799.3335	(M+4)-Br_2/(M+6)-Br_2	0.66-0.98	209
$^{13}C_{12}$-DeBDE	809.3757	811.3737	(M+4)-Br_2/(M+6)-Br_2	0.65-0.94	^{13}C-BDE 209

B. Chlorinated Diphenyl Ethers (CDE)

Compound	Quantification Ions (m/z)		Ion Type	Isotope Ratio	Diphenyl Ethers Monitored
	1st	2nd			
MoCDE	204.0341	206.0312	M/M+2	2.42-3.64	1,2,3
DiCDE	237.9952	239.9922	M/M+2	1.23-1.85	7,8,13,15
TriCDE	271.9562	273.9532	M/M+2	0.82-1.24	32,17,28,33,16,22,37,35
TeCDE	305.9172	307.9143	M/M+2	0.62-0.94	62,75,68,59,49,67,47,74,66,77
$^{13}C_{12}$-TeCDE	317.9574	319.9545	M/M+2	0.62-0.94	^{13}C-CDE 77
PeCDE	269.9406	271.9377	M-Cl_2/(M+2)-Cl_2	0.84-1.26	100,102,119,116,101,99,118,89,85,126,105
HxCDE	303.9016	305.8987	M-Cl_2/(M+2)-Cl_2	0.62-0.94	150,154,147/153,163140,167,137,138,184,156,157,128
$^{13}C_{12}$-HxCDE	315.9419	317.9389	M-Cl_2/(M+2)-Cl_2	0.62-0.94	^{13}C-CDE 156, ^{13}C-CDE 128
HpCDE	339.8598	341.8569	(M+2)-Cl_2/(M+4)-Cl_2	1.24-1.86	184,187,182/171,172,180/181,190,177,170
$^{13}C_{12}$-HpCDE	351.9000	353.8970	(M+2)-Cl_2/(M+4)-Cl_2	1.25-1.87	^{13}C-CDE 170
OcCDE	373.8208	375.8179	(M+2)-Cl_2/(M+4)-Cl_2	0.99-1.49	204,197,203,201,196,194,195
$^{13}C_{12}$-OcCDE	385.8610	387.8581	(M+2)-Cl_2/(M+4)-Cl_2	1.00-1.50	^{13}C-CDE 194
NoCDE	407.7818	409.7789	(M+2)-Cl_2/(M+4)-Cl_2	0.83-1.25	208,207,206
DeCDE	441.7428	443.7399	(M+2)-Cl_2/(M+4)-Cl_2	0.71-1.07	209

APPENDIX X

Pesticide M/Z (SIR) and Isotope Ratio Control Limits

Compounds	Quantification Ions (m/z) 1st	2nd	Ion Type	Isotope Ratio
Fraction 1 / Fraction 2				
1,3,5-trichlorobenzene (TriCB), 1,2,4-TriCB, 1,2,3-TriCB	179.9300	181.9271	M/M+2	0.88-1.20
$^{13}C_6$-1,2,3-TriCB	185.9502	187.9472	M/M+2	0.83-1.25
1,2,3,5-tetrachlorobenzene (TeCB), 1,2,4,5-TeCB, 1,2,3,4-TeCB	213.8911	215.8881	M/M+2	0.62-0.94
$^{13}C_6$-1,2,3,4- TeCB	219.9112	221.9082	M/M+2	0.66-0.90
pentachlorobenzene	249.8491	251.8462	M+2/M+4	1.25-1.87
$^{13}C_6$-pentachlorobenzene	255.8693	257.8663	M+2/M+4	1.33-1.79
alpha-hexachlorocyclohexane (HCH), beta-HCH, gamma-HCH	218.9116	220.9086	(M+1)-Cl_2/(M+3)-Cl_2	1.66-2.50
$^{13}C_6$-gamma-HCH	222.9346	224.9317	(M-1)-Cl_2/(M+1)-Cl_2	0.66-0.90
hexachlorobenzene	283.8102	285.8072	M+2/M+4	1.00-1.50
$^{13}C_6$-hexachlorobenzene	289.8303	291.8273	M+2/M+4	1.06-1.44
heptachlor, trans-chlordane*, trans-nonachlor*, cis-chlordane*	271.8102	273.8072	M-C_5H_3Cl/M-C_5HCl	1.00-1.50
aldrin, oxychlordane*, dieldrin	262.8570	264.8540	M-C_5H_4Cl/M-C_5H_2Cl	1.24-1.86
endosulphan*	238.8990	240.8960	M-$CH_3SO_3Cl_2$/M-$CHSO_3Cl_2$	0.60-0.90
o,p'-DDE[1], p,p'-DDE	246.0003	247.9974	M-Cl_2(M+2)-Cl_2	1.25-1.87
$^{13}C_{12}$-PCB-111	265.9859	267.9829	M-Cl_2/(M+2)-Cl_2	0.88-1.20
$^{13}C_{12}$-p,p'-DDE	258.0405	260.0376	M-Cl_2/(M+2)-Cl_2	1.33-1.79
o,p'-DDD[2], p,p'-DDD, o,p'-DDT[3], p,p'-DDT	235.0081	237.0052	M-$CHCl_2$/(M+1)-Cl_2	1.25-1.87
cis-nonachlor*	235.0081	237.0052	M-$C_5H_5Cl_4$/M-$C_5H_3Cl_4$	1.00-1.50
$^{13}C_{12}$-p,p'-DDT	247.0483	249.0454	M-CCl_3/(M+2)-CCl_3	1.33-1.79
methoxychlor	227.1070	228.1110	M-CCl_3/(M+1)-CCl_3	5.33-7.99
mirex	271.8102	273.8072	(M+2)-C_5Cl_6/(M+4)-C_5Cl_6	1.00-1.50
$^{13}C_8$-mirex	275.8236	277.8206	(M+2)-C_5Cl_6/(M+4)-C_5Cl_6	1.06-1.44
Fraction 3				
hexachlorobenzene*	283.8102	285.8072	M+2/M+4	1.00-1.50
$^{13}C_6$-hexachlorobenzene*	289.8303	291.8273	M+2/M+4	1.33-1.79
heptachlor epoxide	352.8440	354.8410	(M+2)-Cl/(M+4)-Cl	1.00-1.50
oxychlordane	386.8050	388.8020	(M+2)-Cl/(M+4)-Cl	0.83-1.25
trans-chlordane, cis-chlordane	372.8260	374.8230	(M+2)-Cl/(M+4)-Cl	0.83-1.25
trans-nonachlor, cis-nonachlor	406.7870	408.7840	(M+2)-Cl/(M+4)-Cl	0.71-1.07
$^{13}C_{12}$-PCB-111	337.9207	339.9177	M+2/M+4	1.00-1.50

endrin	316.9040	318.9010	(M+2)-COCl/(M+4)-COCl	1.25-1.87
Lock mass	375.9807			

* monitored but not quantified
[1] dichlorodiphenyldichloroethylene
[2] dichlorodiphenyldichloroethane
[3] dichlorodiphenyltrichloroethane

APPENDIX XI

Data Processing

Overview:

Data processing begins after the HRGC/HRMS analysis of the samples. Chromatograms are printed, the data is targeted, and some initial quality assurance (QA) work is done. The data is converted to Excel™ spreadsheet format and processed electronically to print peak lists to facilitate QA work. After QA is done, corrections are made to the data electronically. The data is transferred to a storage spreadsheet, and reports are printed.

MS Data Processing (Targetting) with OPUS/2020:

Targetting filters raw data through the target file, which identifies specific congeners via m/z, retention time and isotope ratio, and quantifies these congeners via the calibration RRF and the input of surrogate and standard amounts. Surrogate and standard amounts must reflect a sample split, e.g., a 70/30 split would require targetting using 70% of the sample weights and 70% of the surrogate internal standard amounts, but with 100% of the surrogate recovery standard amount.

Preliminary QA:

1. High Intensities: Samples with chromatogram peak intensities > $3 * 10^8$ counts must be diluted for reanalysis as detector saturation as occurred. The concentrated sample data undergoes QA fully except for the overheight congeners, which are quantified using the diluted sample analysis data.
2. Carryover: Samples that show a 5% contribution from the preceding sample due to carryover during analysis, must be reanalysed. The extent of the carryover is based on that observed in the toluene proceeding the CS3 standard for that particular MS batch.

3. High Recoveries: A record of samples showing >120% surrogate internal standard recoveries must be made. Possible reasons for high % recoveries are:

a) An impurity coeluting or partially coeluting with the surrogate will increase apparent recoveries; correction would involve adjustments to the surrogate internal standard peak area.
b) Detector saturation caused by natives with high counts (peak intensities > $1*10^8$) and approximately 1000X greater than the surrogate counts can result in interference among m/z channels and lead to elevated % recoveries. Dilution and respiking should solve this problem.

c) Saturation of the ion chamber due to some other impurity could cause error in % recoveries. If the impurity has a mass close to that of the lock mass ion then the monitored lock mass intensity will show a pronounced increase as the MS will lock on the impurity signal, attributing it erroneously to the calibrant. If the impurity has a mass very different than the lock mass ion, the monitored lock mass intensity will show a pronounced decrease as the impurity dilutes the calibrant in the ion chamber, but is invisible to the detector. In this case further cleanup of the sample would be necessary.

Data processing with Contaminants Data Analysis System (CDAS):

The 2020™ data is converted to Excel™ spreadsheet format. This step is carried out from Opus™, using Excursion™ on a networked PC. Once connected the CDAS software converts data either individually or in batches (Puritch and Soderquist, 1995). Once this step is completed, the data will be in v:\export, and each 2020™ file will exist as several Excel™ files with the extensions: .xsm, .x01, x02, etc.

After QA of the printed reports, any necessary corrections are made to the electronic version. The data are then transferred to storage spreadsheets using the Export2.xls software, and formatted and checked for errors using the IOSFormat2.xls software. The final step is the production of the client report from the appropriate merge file.

APPENDIX XII

Samples of Data Release Forms

A. Dioxin/Furan Sample Data Sheet

Sample: Proc Blk - Avg
Sample Type: Procedural Blank
Laboratory: I.O.S. Regional Contaminants Laboratory
Site: N/A
Sampling Date: N/A
Sample Processing Date: N/A
Sample Wt. Submitted for Analysis (g): N/A

Sample Net Wt. Extracted (g): 10.00
GC Column & MS: DB5-60m Autospec
% Lipid: N/A
% Moisture: N/A
Initial Calibration Date: N/A
Analysis Date: N/A
File #: N/A

Congener	pg/g	DL	TEQ**	Homologue	pg/g	DL	NP
2,3,7,8-TCDD	ND	0.08		TCDD	ND	0.08	0
1,2,3,7,8-PeCDD*	ND	0.08		PeCDD	ND	0.08	0
1,2,3,4,7,8-HxCDD*	ND	0.10		HxCDD	0.27	0.10	2
1,2,3,6,7,8-HxCDD*	0.15	0.10		HpCDD	ND	0.12	0
1,2,3,7,8,9-HxCDD*	ND	0.10		OCDD0.26	0.14		
1,2,3,4,6,7,8-HpCDD	ND	0.12					
OCDD	0.26	0.14		Total PCDD	0.53		
2,3,7,8-TCDF	ND	0.05		TCDF	0.09	0.05	1
1,2,3,7,8-PeCDF*	ND	0.06		PeCDF	ND	0.06	0
2,3,4,7,8-PeCDF*	ND	0.06		HxCDF	ND	0.08	0
1,2,3,4,7,8-HxCDF*	ND	0.08		HpCDF	0.11	0.10	1
1,2,3,6,7,8-HxCDF*	ND	0.08		OCDFND	0.12		
2,3,4,6,7,8-HxCDF*	ND	0.08					
1,2,3,7,8,9-HxCDF*	ND	0.08		Total PCDF	0.20		
1,2,3,4,6,7,8-HpCDF	ND	0.10					
1,2,3,4,7,8,9-HpCDF	ND	0.10					
OCDF	ND	0.12					
				Total TEQ**			

Surrogate	Amount Added (pg)	% Recovery
$^{13}C_{12}$-2,3,7,8-TCDD	1007	89
$^{13}C_{12}$-1,2,3,7,8-PeCDD	1007	101
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	1007	68
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	1007	89
$^{13}C_{12}$-OCDD	2013	89
$^{13}C_{12}$-2,3,7,8-TCDF	1007	85
$^{13}C_{12}$-1,2,3,7,8-PeCDF	1007	89
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	1007	74
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	1007	77

Note: (1) Results are corrected for surrogate recovery
(2) DL = detection limit (pg/g/analyte peak)
(3) ND = not detected
(4) NP = total number of analyte peaks not including NDR(s)
(5) N/A = not applicable
(6) NDR = not detected due to incorrect isotopic ratio
(7) NDR concentrations are included in total TEQ
(8) pg/g values in brackets are not taken into account for the totals calculations
(9) * Value represents maximum possible amount as this isomer could coelute with other isomer(s)
(10) **Maximum. Based on TEF values acceptable to Health Canada

Approved by:_____ Date: _____
Michael G. Ikonomou

B. Non-ortho (NO) - PCBs Sample Data Sheet

Sample: Proc Blk - Avg
Sample Type: Procedural Blank
Laboratory: I.O.S. Regional Contaminants Laboratory
Site: N/A.
Sampling Date: N/A
Sample Processing Date: N/A
Sample Wt. Submitted for Analysis (gm): N/A

Sample Net Wt. Extracted (g): 10.00
GC Column & MS: DB5-60m Autospec
% Lipid: N/A
% Moisture: N/A
Initial Calibration Date: N/A
Analysis Date: N/A
File #: N/A

Congener	pg/g	DL	TEQ**
3,5-DiCB (PCB 14)*	ND	0.14	
3,3'-DiCB (PCB 11)	2.42	0.14	
3,4-DiCB (PCB 12)*	ND	0.14	
3,4'-DiCB (PCB 13)	0.53	0.14	
4,4'-DiCB (PCB 15)	4.64	0.14	
Total Coplanar DiCB	7.59		
3,3',5-TrCB (PCB 36)*	ND	0.09	
3,4',5-TrCB (PCB 39)	ND	0.09	
3,4,5-TrCB (PCB 38)*	0.13	0.09	
3,3',4-TrCB (PCB 35)	0.59	0.09	
3,4,4'-TrCB (PCB 37)	18.42	0.09	
Total Coplanar TrCB	19.14		
3,3',5,5'-TeCB (PCB 80)	0.99	0.04	
3,3',4,5'-TeCB (PCB 79)	ND	0.04	
3,3',4,5-TeCB (PCB 78)	ND	0.04	
3,4,4',5-TeCB (PCB 81)	0.15	0.04	
3,3',4,4'-TeCB (PCB 77)	2.51	0.04	
Total Coplanar TeCB	3.65		
3,3',4,5,5'-PeCB (PCB 127)	0.36	0.04	
3,3',4,4',5-PeCB (PCB 126)	0.15	0.04	
Total Coplanar PeCB	0.51		
3,3',4,4',5,5'-HxCB (PCB 169)	0.08	0.04	
Total Coplanar HxCB	0.08		
Total TEQ			

Surrogate	Amount Added (pg)	% Recovery
$^{13}C_{12}$-4,4'-DiCB (PCB 15)	985	35
D_5-3,4,5-TrCB (PCB 38)	948	42
$^{13}C_{12}$-3,3',4,4'-PeCB (PCB 77)	987	63
$^{13}C_{12}$-3,3',4,4',5-PeCB (PCB 126)	993	71
$^{13}C_{12}$-3,3',4,4',5,5'-HxCB (PCB 169)	994	60
$^{13}C_{12}$-2,2',4,5,5'-PeCB (PCB 101)	991	Recovery Standard

Note: (1) Results are corrected for surrogate recovery
(2) ND = not detected
(3) DL = detection limit (pg/g/analyte peak)
(4) N/A = not applicable
(5) NDR = not detected due to incorrect isotopic ratio
(6) NDR concentrations are included in total TEQ
(7) pg/g values in brackets are not taken into account for the totals calculations
(8) * Calculated elution times using reference: Mullin, et al., *Environ. Sci. and Technol.*, **1984**, *18*, 468-476
(9) ** Based on TEF values acceptable to Health Canada

Approved by:_____ Date: _____

C. Mono-Ortho PCBs Sample Data Sheet

Sample: Proc Blk - Avg
Sample Type: Procedural Blank.
Laboratory: I.O.S. Regional Contaminants Laboratory
Site: N/A.
Sampling Date: N/A
Sample Processing Date: N/A
Sample Wt. Submitted for Analysis (gm): N/A

Sample Net Wt. Extracted (g): 10.00
GC Column & MS: DB5-60m Autospec
% Lipid: N/A
% Moisture: N/A
Initial Calibration Date: N/A
Analysis Date: N/A
File #: N/A

Congener	pg/g	DL
2,4-DiCB (PCB 7)*/		
2,5-DiCB (PCB 9)*	0.3	1.7
2,3'-DiCB (PCB 6)*	0.5	1.7
2,4'-DiCB (PCB 8)/		
2,3-DiCB (PCB 5)*	3.5	1.7
Total Mono-Ortho DiCB	4.3	
2,3,5-TrCB (PCB 23)*	ND	0.2
2',3,5-TrCB (PCB 34)*	ND	0.2
2,4,5-TrCB (PCB 29)*	ND	0.2
2,3',5-TrCB (PCB 26)*	1.7	0.2
2,3',4-TrCB (PCB 25)*	1.0	0.2
2,4',5-TrCB (PCB 31)	14.2	0.2
2,4,4'-TrCB (PCB 28)	22.8	0.2
2,3,4-TrCB (PCB 21)*	ND	0.2
2',3,4-TrCB (PCB 33)*/		
2,3,3'-TrCB (PCB 20)*	11.4	0.2
2,3,4'-TrCB (PCB 22)*	6.2	0.2
Total Mono-Ortho TrCB	57.4	
2,3',5,5'-TeCB (PCB 72)*	ND	0.1
2,3',4,5'-TeCB (PCB 68)*	ND	0.1
2,3,3',5-TeCB (PCB 57)*	ND	0.1
2,3',4,5-TeCB (PCB 67)*	0.3	0.1
2,3,3',5'-TeCB (PCB 58)	ND	0.1
2,3,4',5-TeCB (PCB 63)*	0.2	0.1
2,3,4,5-TeCB (PCB 61)/		
2,4,4',5-TeCB (PCB 74)	4.1	0.1
2,3',4',5-TeCB (PCB 70)/		
2',3,4,5-TeCB (PCB 76)*	8.0	0.1
2,3',4,4'-TeCB (PCB 66)	7.3	0.1
2,3,3',4-TeCB (PCB 55)*	0.2	0.1
2,3,3',4'-TeCB (PCB 56)*/		
2,3,4,4'-TeCB (PCB 60)	5.5	0.1
Total Mono-Ortho TeCB	25.6	

Congener	pg/g	DL
2,3,3',5,5'-PeCB (PCB 111)*	ND	0.1
2,3',4,5,5'-PeCB (PCB 120)*	ND	0.1
2',3,4,5,5'-PeCB (PCB 124)	0.3	0.1
2,3,3',4,5'-PeCB (PCB 108)/		
2,3,3',4',5-PeCB (PCB 107)*	0.5	0.1
2',3,4,4',5-PeCB (PCB 123)	0.2	0.1
2,3',4,4',5-PeCB (PCB 118)	8.7	0.1
2,3,4,4',5-PeCB (PCB 114)	0.3	0.1
2',3,3',4,5-PeCB (PCB 122)	ND	0.1
2,3,3',4,4'-PeCB (PCB 105)	4.0	0.1
Total Mono-Ortho PeCB	14.0	
2,3,3',4,5,5'-HxCB (PCB 159)	ND	0.1
2,3,3',4',5,5'-HxCB (PCB 162)	ND	0.1
2,3',4,4',5,5'-HxCB (PCB 167)	0.3	0.1
2,3,3',4,4',5-HxCB (PCB 156)	1.0	0.1
2,3,3',4,4',5'-HxCB (PCB 157)	0.9	0.1
Total Mono-Ortho HxCB	2.2	
2,3,3',4,4',5,5'-HpCB (PCB 189)	ND	0.1
Total Mono-Ortho HpCB	ND	

Surrogate	Amount Added (pg)	% Recovery
$^{13}C_{12}$-2,4,4'-TrCB (PCB 28)	1425	22
$^{13}C_{12}$-2,3',4,4',5-PeCB (PCB 118)	1477	52
$^{13}C_{12}$-2,3,3',4,4'-PeCB (PCB 105)	1500	55
$^{13}C_{12}$-2,3,3',4,4',5-HxCB (PCB 156)	1498	43
$^{13}C_{12}$-2,2',4,5,5'-PeCB (PCB 101)	1489	Recovery Standard

Note: (1) Results are corrected for surrogate recovery
(2) ND = not detected
(3) DL = detection limit (pg/g/analyte peak)
(4) N/A = not applicable
(5) NDR = not detected due to incorrect isotopic ratio
(6) pg/g values in brackets are not taken into account for the totals calculations
(7) * Calculated elution times using reference: Mullin, et al., *Environ. Sci. and Technol.*, **1984**, *18*, 468-476

Approved by:_____ Date: _____

D. Di/Tri/Tetra-Ortho (DO) - PCBs Sample Data Sheet

Sample: Proc Blk - Avg
Sample Type: Procedural Blank
Laboratory: I.O.S. Regional Contaminants Laboratory
Site: N/A
Sampling Date: N/A
Sample Processing Date: N/A
Sample Wt. Submitted for Analysis (gm): N/A

Sample Net Wt. Extracted (g): 10.00
GC Column & MS: DB5-60m Autospec
% Lipid: N/A
% Moisture: N/A
Initial Calibration Date: N/A
Analysis Date: N/A
File #: N/A

Congener	pg/g	DL
2,6-DiCB (PCB10)* /		
2,2'-DiCB (PCB 4)	1.8	0.9
Total Di-Ortho DiCB	1.8	
2,2',6-TriCB (PCB 19)*	ND	0.9
2,4,6-TriCB (PCB 30)*	ND	0.9
2,2',5-TriCB (PCB 18)	6.3	0.9
2,2',4-TriCB (PCB 17)*	3.4	0.9
2,3',6-TriCB (PCB 27)/		
2,3,6-TriCB (PCB 24)	ND	0.9
2,2',3-TriCB (PCB 16)*/		
2,4',6-TriCB (PCB 32)*	7.4	0.9
Total Di-Ortho TriCB	17.1	
2,2',6,6'-TeCB (PCB 54)*	ND	0.9
2,2',4,6-TeCB (PCB 50)*	ND	0.9
2,2',5,6'-TeCB (PCB 53)*	ND	0.9
2,2',4,6'-TeCB (PCB 51)*	ND	0.9
2,2',3,6-TeCB (PCB 45)	0.9	0.9
2,2',3,6'-TeCB (PCB 46)	ND	0.9
2,3',4,6-TeCB (PCB 69)*	ND	0.9
2,3',5',6-TeCB (PCB 73)* /		
2,2',5,5'-TeCB (PCB 52)	9.4	0.9
2,2',3,5-TeCB (PCB 43)*	ND	0.9
2,2',4,5'-TeCB (PCB 49)	5.8	0.9
2,2',4,4'-TeCB (PCB 47)/		
2,4,4',6-TeCB (PCB 75)*/		
2,2',4,5-TeCB (PCB 48)*	4.4	0.9
2,3,5,6-TeCB (PCB 65)*	ND	0.9
2,3,4,6-TeCB (PCB 62)*	ND	0.9
2,2',3,5'-TeCB (PCB 44)	8.7	0.9
2,3,3',6-TeCB (PCB 59)*/		
2,2',3,4'-TeCB (PCB 42)	4.3	0.9
2,3',4',6-TeCB (PCB 71)* /		
2,2',3,4-TeCB (PCB 41)/		
2,3,4',6-TeCB (PCB 64)*	12.3	0.9
2,2',3,3'-TeCB (PCB 40)*	1.3	0.9
Total Di-Ortho TeCB	47.1	
2,2',4,6,6'-PeCB (PCB 104)*	ND	0.9
2,2',3,6,6'-PeCB (PCB 96)*	ND	0.9
2,2',4,5',6-PeCB (PCB 103)*	ND	0.9
2,2',4,4',6-PeCB (PCB 100)*	ND	0.9
2,2',3,5,6'-PeCB (PCB 94)*	ND	0.9
2,2',3',4,6-PeCB (PCB 98)*	ND	0.9
2,2',4,5,6'-PeCB (PCB 102)* /		
2,2',3,5,6-PeCB (PCB 93)*	0.9	0.9
2,2',3,5',6-PeCB (PCB 95)	6.7	0.9
2,2',3,4,6-PeCB (PCB 88)*	ND	0.9
2,3',4,5',6-PeCB (PCB 121)*	ND	0.9
2,2',3,4',6-PeCB (PCB 91)	ND	0.9
2,2',3,5,5'-PeCB (PCB 92)*/		
2,2',3,3',6-PeCB (PCB 84)	1.3	0.9
2,2',3,4,6'-PeCB (PCB 89)*	1.6	0.9
2,2',4,5,5'-PeCB (PCB 101)/		
2,2',3,4',5-PeCB (PCB 90)	10.4	0.9
2,3,3',5',6-PeCB (PCB 113)*	ND	0.9
2,2',4,4',5-PeCB (PCB 99)	4.3	0.9
2,3',4,4',6-PeCB (PCB 119)	ND	0.9
2,3,3',5,6-PeCB (PCB 112)*	ND	0.9
2,3,3',4,6-PeCB (PCB 109)*/		
2,2',3,3',5-PeCB (PCB 83)*	ND	0.9
2,2',3',4,5-PeCB (PCB 97)/		
2,2',3,4,5-PeCB (PCB 86)*	2.5	0.9
2,3,4,5,6-PeCB (PCB 116)*/		
2',3,4,5,6'-PeCB (PCB 125)/		
2,3,4',5,6-PeCB (PCB 117)*	ND	0.9
2,3,4,4',6-PeCB (PCB 115)*/		
2,2',3,4,5'-PeCB (PCB 87)	4.3	0.9
2,2',3,4,4'-PeCB (PCB 85)	1.6	0.9
2,3,3',4',6-PeCB (PCB 110)	7.9	0.9
2,2',3,3',4-PeCB (PCB 82)	ND	0.9
Total Di-Ortho PeCB	41.5	
2,2',4,4',6,6'-HxCB (PCB 155)*	ND	0.9
2,2',3,4',6,6'-HxCB (PCB 150)*	ND	0.9
2,2',3,5,6,6'-HxCB (PCB 152)*	ND	0.9
2,2',3,4,6,6'-HxCB (PCB 145)*	ND	0.9
2,2',3,4',5,6'-HxCB (PCB 148)*	ND	0.9
2,2',3,3',6,6'-HxCB (PCB 136)*	2.6	0.9
2,2',4,4',5,6'-HxCB (PCB 154)*	ND	0.9
2,2',3,5,5',6-HxCB (PCB 151)	4.4	0.9
2,2',3,3',5,6'-HxCB (PCB 135)*/		
2,2',3,4,5',6-HxCB (PCB 144)	2.5	0.9
2,2',3,4',5,6-HxCB (PCB 147)*	ND	0.9
2,2',3,4',5',6-HxCB (PCB 149)	12.8	0.9
2,2',3,4,4',6-HxCB (PCB 139)* /		
2,2',3,4,4',6'-HxCB (PCB 140)*	ND	0.9
2,2',3,4,5,6'-HxCB (PCB 143)* /		
2,2',3,3',5,6-HxCB (PCB 134)*	ND	0.9
2,2',3,4,5,6-HxCB (PCB 142)* /		
2,2',3,3',4,6-HxCB (PCB 131)	ND	0.9
2,2',3,3',5,5'-HxCB (PCB 133)*	ND	0.9
2,3,3',5,5',6-HxCB (PCB 165)*	ND	0.9
2,2',3,4',5,5'-HxCB (PCB 146)/		
2,3,3',4,5',6-HxCB (PCB 161)*	1.5	0.9
2,2',3,3',4,6'-HxCB (PCB 132)*/		
2,2',4,4',5,5'-HxCB (PCB 153)	16.2	0.9
2,3',4,4',5',6-HxCB (PCB 168)	2.4	0.9
2,2',3,4,5,5'-HxCB (PCB 141)	2.6	0.9
2,2',3,4,4',5-HxCB (PCB 137)	ND	0.9
2,2',3,3',4,5'-HxCB (PCB 130)	ND	0.9
2,3,3',4,5,6-HxCB (PCB 160)*/		
2,3,3',4',5,6-HxCB (PCB 163)* /		
2,3,3',4',5',6-HxCB (PCB 164)* /		
2,2',3,4,4',5'-HxCB (PCB 138)	14.0	0.9
2,3,3',4,4',6-HxCB (PCB 158)	1.1	0.9
2,2',3,3',4,5-HxCB (PCB 129)*	ND	0.9
2,3,4,4',5,6-HxCB (PCB 166)*	ND	0.9
2,2',3,3',4,4'-HxCB (PCB 128)	1.3	0.9
Total Di-Ortho HxCB	60.1	

Congener	pg/g	DL	Congener	pg/g	DL
2,2',3,4',5,6,6'-HpCB (PCB 188)*	ND	0.9	2,2',3,3',5,5',6,6'-OctCB (PCB 202)*	ND	0.9
2,2',3,4,4',6,6'-HpCB (PCB 184)*	ND	0.9	2,2',3,3',4,5',6,6'-OctCB (PCB 200)	ND	0.9
2,2',3,3',5,6,6'-HpCB (PCB 179)	1.7	0.9	2,2',3,4,4',5,6,6'-OctCB (PCB 204)*	ND	0.9
2,2',3,3',4,6,6'-HpCB (PCB 176)*	ND	0.9	2,2',3,3',4,4',6,6'-OctCB (PCB 197)	ND	0.9
2,2',3,4,5,6,6'-HpCB (PCB 186)*	ND	0.9	2,2',3,3',4,5,6,6'-OctCB (PCB 199)	ND	0.9
2,2',3,3',5,5',6-HpCB (PCB 178)	ND	0.9	2,2',3,3',4,5,5',6-OctCB (PCB 198)*	ND	0.9
2,2',3,3',4,5',6-HpCB (PCB 175)	ND	0.9	2,2',3,3',4',5,5',6-OctCB (PCB 201)*	2.3	0.9
2,2',3,4',5,5',6-HpCB (PCB 187)/			2,2',3,4,4',5,5',6-OctCB (PCB 203)/		
2,2',3,4,4',5,6'-HpCB (PCB 182)	7.4	0.9	2,2',3,3',4,4',5',6-OctCB (PCB 196)	1.9	0.9
2,2',3,4,4',5',6-HpCB (PCB 183)	2.3	0.9	2,2',3,3',4,4',5,6-OctCB (PCB 195)*	ND	0.9
2,2',3,4,5,5',6-HpCB (PCB 185)	ND	0.9	2,2',3,3',4,4',5,5'-OctCB (PCB 194)	ND	0.9
2,2',3,3',4,5,6'-HpCB (PCB 174)/			2,3,3',4,4',5,5',6-OctCB (PCB 205)	ND	0.9
2,2',3,4,4',5,6-HpCB (PCB 181)*	4.4	0.9	**Total Di-Ortho OctCB**	4.2	
2,2',3,3',4',5,6-HpCB (PCB 177)	2.1	0.9			
2,2',3,3',4,4',6-HpCB (PCB 171)	ND	0.9	2,2',3,3',4,5,5',6,6'-NonCB (PCB 208)	ND	0.9
2,2',3,3',4,5,6-HpCB (PCB 173)*	ND	0.9	2,2',3,3',4,4',5,6,6'-NonCB (PCB 207)*	ND	0.9
2,3,3',4,5,5',6-HpCB (PCB 192)*/			2,2',3,3',4,4',5,5',6-NonCB (PCB 206)	ND	0.9
2,2',3,3',4,5,5'-HpCB (PCB 172)	ND	0.9	**Total Di-Ortho NonCB**	ND	
2,2',3,4,4',5,5'-HpCB (PCB 180)	6.9	0.9			
2,3,3',4',5,5',6-HpCB (PCB 193)	ND	0.9	DecCB (PCB 209)	ND	0.9
2,3,3',4,4',5',6-HpCB (PCB 191)*	ND	0.9	**Total Di-Ortho DecCB**	ND	
2,2',3,3',4,4',5-HpCB (PCB 170)/					
2,3,3',4,4',5,6-HpCB (PCB 190)*	1.9	0.9			
Total Di-Ortho HpCB	26.7				

Surrogate	Amount Added (pg)	% Recovery
$^{13}C_{12}$-2,2',5,5'-TeCB (PCB 52)	1943	35
$^{13}C_{12}$-2,2',4,5,5'-PeCB (PCB 101)	2070	57
$^{13}C_{12}$-2,2',3,3',4,4'-HxCB (PCB 128)	2012	58
$^{13}C_{12}$-2,2',3,4,4',5,5'-HpCB (PCB 180)	1944	72
$^{13}C_{12}$-2,2',3,3',4,4',5,5'-OctCB (PCB 194)	1996	71
$^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-NonCB (PCB 208)	1967	84
$^{13}C_{12}$-22',3,3',4,4',5,5',6,6'-DecCB (PCB 209)	1971	84
$^{13}C_{12}$-2,3,3',5,5'-PeCB (PCB 111)	2017	Recovery Standard

Note:
(1) Results are corrected for surrogate recovery
(2) DL = detection limit (pg/g/analyte peak)
(3) ND = not detected
(4) NDR = not detected due to incorrect isotopic ratio
(5) N/A = not applicable
(6) pg/g values in brackets are not taken into account for the totals calculations
(7) PCB assignments based on Ballschmiter, K. and Zell, M., *Fresenius Z. Anal. Chem.*, **1980**, *302*,20-31
(8) * Calculated elution times using reference: Mullin, et al., *Environ. Sci. and Technol.*, **1984**, *18*, 468-47

Approved by:_____ Date: _____

E. Bromo-Diphenyl Ether Sample Data Sheet

Sample: Proc Blk – Avg
Sample Type: Procedural Blank
Laboratory: I.O.S. Regional Contaminants Laboratory
Site: N/A
Sampling Date: N/A
Sample Processing Date: N/A
Sample Wt. Submitted for Analysis (gm): N/A

Sample Net Wt. Extracted (g): 10.00
GC Column & MS: DB5-60m Autospec
% Lipid: N/A
% Moisture: N/A
Initial Calibration Date: N/A
Analysis Date: N/A
File #: N/A

Congener	pg/g	DL	Congener	pg/g	DL
2-MoBDE (1)	ND	0.6	unknown PeBDE(1) (rrt:1.0116)*	ND	0.2
3-MoBDE(2)	ND	0.6	unknown PeBDE(2) (rrt:1.0179)*	ND	0.2
4-MoBDE(3)	ND	0.6	unknown PeBDE(3) (rrt:1.0214)*	ND	0.2
			unknown PeBDE(4) (rrt:1.0344)*	ND	0.2
			unknown PeBDE(5) (rrt:1.0402)*	ND	0.2
2,6-DiBDE (10)	ND	0.1	unknown PeBDE(6) (rrt:1.0446)*	ND	0.2
2,4-DiBDE (7)	ND	0.1	unknown PeBDE(7) (rrt:1.0625)*	ND	0.2
2,4'-DiBDE (11)/			unknown PeBDE(8) (rrt: 1.0661)*	ND	0.2
3,3'-DiBDE (8)	ND	0.1	unknown PeBDE(9) (rrt: 1.0746)*	ND	0.2
3,4-DiBDE (12)	ND	0.1	unknown PeBDE(10) (rrt: 1.0804)*	ND	0.2
3,4'-DiBDE (13)	ND	0.1			
4,4'-DiBDE (15)	ND	0.1	2,2',4,4',6,6'-HxBDE (155)	ND	0.3
			2,2',4,4',5,6'-HxBDE (154)	0.6	0.3
2,4,6-TrBDE (30)	ND	0.1	2,2',4,4',5,5'-HxBDE (153)	1.8	0.3
2,4',6-TrBDE (32)	ND	0.1	2,2',3,4,4',6'-HxBDE (140)	ND	0.3
2,2',4-TrBDE (17)	0.2	0.1	2,2',3,4,4',5'-HxBDE (138)/		
2,3',4-TrBDE (25)	ND	0.1	2,3,4,4',5,6-HxBDE (166)	ND	0.3
2,4,4'-TrBDE (28)/			unknown HxBDE(1) (rrt: 1.1612)*	ND	0.3
2',3,4-TrBDE (33)	NDR(0.5)	0.1	unknown HxBDE(2) (rrt: 1.1683)*	ND	0.3
3,3',4-TrBDE (35)	ND	0.1			
3,4,4'-TrBDPE (37)	ND	0.1			
unknown TrBDE(1) (rrt:0.7201)*	ND	0.1	2,2',3,4,4',5',6-HpBDE (183)	6.1	0.5
unknown TrBDE(2) (rrt:0.7848)*	ND	0.1	unknown HpBDE III	ND	0.5
			unknown HpBDE IV	0.7	0.5
			2,2',3,4,4',5,6-HpBDE (181)	ND	0.5
2,4,4',6-TeBDE (75)	ND	0.2	2,3,3',4,4',5,6-HpBDE (190)	ND	0.5
2,2',4,5'-TeBDE (49)	0.5	0.2		6.8	
2,3',4',6-TeBDE (71)	ND	0.2			
2,2',4,4'-TeBDE (47)	10.5	0.2	unknown OcBDE I	0.7	0.4
2,3',4,4'-TeBDE (66)	0.3	0.2	unknown OcBDE II	4.0	0.4
3,3',4,4'-TeBDE (77)	ND	0.2	unknown OcBDE III	2.7	0.4
			unknown OcBDE IV	3.5	0.4
			unknown OcBDE(1) (rrt: 1.3089)*	ND	0.4
2,2',4,4',6-PeBDE (100)	1.6	0.2			
2,3',4,4',6-PeBDE (119)	1.3	0.2			
2,2',4,4',5-PeBDE (99)	5.5	0.2	2,2',3,3',4,5,5',6,6'-NoBDE (208)	1.7	0.6
2,3,4,5,6-PeBDE (116)	ND	0.2	2,2',3,3',4,4',5,6,6'-NoBDE (207)	8.0	1.9
2,2',3,4,4'-PeBDE (85)	0.5	0.2	2,2',3,3',4,4',5,5',6-NoBDE (206)	24.5	5.7
3,3',4,4',5-PeBDE (126)	ND	0.2			
2,3,3',4,4'-PeBDE (105)	ND	0.2	2,2',3,3',4,4',5,5',6,6'-DeBDE (209)	19.9	2.9

Surrogate	Amount Added (pg)	% Recovery
13C-2,4,4'-TrBDE (28)	3260	35
13C-2,2',4,4'-TeBDE (47)	2500	49
13C-2,2',4,4',6-PeBDE (100)	3750	51
13C-2,2',4,4',5-PeBDE (99)	3750	43
13C-3,3',4,4',5-PeBDE (126)	3750	54
13C-2,2',4,4',5,6'-HxBDE (154)	3260	70
13C-2,2',3,4,4',5',6-HpBDE (183)	3260	60
13C-2,2',3,3',4,4',5,5',6,6'-DeBDE (209)	12360	35
13C-3,3',4,4'- TeBDPE (77)		Recovery Standard

Note: (1) Results are corrected for surrogate recovery
(2) ND = not detected
(3) NDR = not detected due to incorrect isotopic ratio
(4) DL = detection limit (pg/g/analyte peak)
(5) N/A = not applicable
(6) * relative retention time (rrt) relative to recovery standard

Approved by:_____ Date: _____

F. Chloro-Diphenyl Ether Sample Data Sheet

Sample: Proc Blk - Avg
Sample Type: Procedural Blank
Laboratory: I.O.S. Regional Contaminants Laboratory
Site: N/A
Sampling Date: N/A
Sample Processing Date: N/A
Sample Wt. Submitted for Analysis (gm): N/A

Sample Net Wt. Extracted (gm): 10.00
GC Column & MS: DB5-60m Autospec
% Lipid: N/A
% Moisture: N/A
Initial Calibration Date: N/A
Analysis Date: N/A
File #: N/A

Congener	pg/g	DL
2-MoCDPE (1)	ND	4.5
3-MoCDPE (2)*	ND	4.5
4-MoCDPE(3)	ND	4.5
2,4-DiCDPE (7)	ND	20.3
2,4'-DiCDPE (8)	ND	20.3
3,4'-DiCDPE (13)*	ND	20.3
4,4'-DiCDPE (15)	ND	20.3
2,4',6-TrCDPE (32)*	ND	22.4
2,2',4-TrCDPE (17)	ND	22.4
2,4,4'-TrCDPE (28)	ND	22.4
2',3,4-TrCDPE (33)	ND	22.4
2,2',3-TrCDPE (16)*	ND	22.4
2,3,4'-TrCDPE (22)*	ND	22.4
3,4,4'-TrCDPE (37)*	ND	22.4
3,3',4-TrCDPE (35)	ND	22.4
2,3,4,6-TeCDPE (62)*	ND	20.7
2,4,4',6-TeCDPE (75)	ND	20.7
2,3',4,5'-TeCDPE (68)*	ND	20.7
2,2',4,6'-TeCDPE (51)*	ND	20.7
2,2',4,5'-TeCDPE (49)*	ND	20.7
2,3',4,5-TeCDPE (67)	ND	20.7
2,3',4',6-TeCDPE (71)	ND	20.7
2,2',4,4'-TeCDPE (47)	ND	20.7
2,4,4',5-TeCDPE (74)	ND	20.7
2,3',4,4'-TeCDPE (66)	ND	20.7
3,3',4,4'-TeCDPE (77)	ND	20.7
2,2',4,4',6-PeCDPE (100)	ND	1.5
2,3',4,4',6-PeCDPE (119)	ND	1.5
2,2',4,5,5'-PeCDPE (101)	ND	1.5
2,3,4,5,6-PeCDPE (116)*	ND	1.5
2,2',3,4',5-PeCDPE (90)*	ND	1.5
2,2',4,4',5-PeCDPE (99)	ND	5.0
2,3',4,4',5-PeCDPE (118)	17.5	5.0
2,2',3,4,6'-PeCDPE (89)*	ND	5.0
2,2',3,4,4'-PeCDPE (85)	7.5	5.0
3,3',4,4',5-PeCDPE (126)	ND	5.0
2,3,3',4,4'-PeCDPE (105)	ND	5.0
2,2',3,4',6,6'-HxCDPE (150)*	ND	3.5
2,2',4,4',5,6'-HxCDPE (154)	ND	3.5
2,2',3,4',5,6-HxCDPE (147)*/ 2,2',4,4',5,5'-HxCDPE (153)	ND	3.5

Congener	pg/g	DL
2,3,3',4',5,6-HxCDPE (163)*	ND	3.5
2,2',3,4,4',6'-HxCDPE (140)	ND	3.5
2,3',4,4',5,5'-HxCDPE (167)	ND	3.5
2,2',3,4,4',5-HxCDPE (137)	ND	3.5
2,2',3,4,4',5'-HxCDPE (138)	ND	3.5
2,3,3',4,4',5-HxCDPE (156)	ND	3.5
2,3,3',4,4',5'-HxCDPE (157)	ND	3.5
2,2',3,3',4,4'-HxCDPE (128)	NDR(4.3)	3.5
2,2',3, 4,4',6,6'-HpCDPE (184)	ND	2.6
2,2',3,4',5,5',6-HpCDPE (187)	ND	2.6
2,2',3, 4,4',5,6'-HpCDPE (182)*/ 2,2',3,3',4,4',6-HpCDPE (171)	ND	2.6
2,2',3,3',4,5,5'-HpCDPE (172)	NDR(4.1)	2.6
2,2',3,4,4',5,6-HpCDPE (181)*	ND	2.6
2,2',3, 4,4',5,5'-HpCDPE (180)	3.7	2.6
2,3,3',4,4',5,6-HpCDPE (190)*	ND	2.6
2,2',3,3',4',5,6-HpCDPE (177)	ND	2.6
2,2',3,3',4,4',5-HpCDPE (170)	10.8	2.6
2,2',3,4,4',5,6,6'-OcCDPE (204)*	ND	2.1
2,2',3,3',4,4',6,6'-OctCDPE (197)*	ND	2.1
2,2',3,4,4',5,5',6-OctCDPE (203)*	ND	2.1
2,2',3,3',4,5,5',6'-OctCDPE (201)	4.5	2.1
2,2',3,3',4,4',5',6-OctCDPE (196)	4.6	2.1
2,2',3,3',4,4',5,5'-OctCDPE (194)	10.0	2.1
2,2',3,3',4,4',5,6-OctCDPE (195)	4.9	2.1
2,2',3,3',4,4',5,5',6-NonCDPE (208)*	ND	2.1
2,2',3,3',4,4',5,6,6'-NonCDPE (207)*	ND	2.1
2,2',3,3',4,4',5,5',6-NonCDPE (206)*	ND	2.1
2,2',3,3',4,4',5,5',6,6'-DeCDPE (209)	ND	8.6

Homologue	pg/g	DL	N
MoCDPE	ND	4.5	
DiCDPE	ND	20.3	
TrCDPE	ND	22.4	
TeCDPE	ND	20.7	
PeCDPE	25.0	3.3	
HxCDPE	ND	3.5	
HpCDPE	14.5	2.6	
OcCDPE	2.4	2.1	
NoCDPE	ND	2.1	
DeCDPE	ND	8.6	

Surrogate	Amount Added (pg)	% Recovery
$^{13}C_{12}$-3,3',4,4'-TeCDPE (77)	1000	16
$^{13}C_{12}$-2,3,3',4,4',5-HxCDPE (156)	2000	42
$^{13}C_{12}$-2,2',3,3',4,4',5-HpCDPE (170)	2000	64
$^{13}C_{12}$-2,2',3,3',4,4',5,5'-OctCDPE (194)	3000	63
$^{13}C_{12}$-2,2',3,3',4,4'- HxCDPE (128)	1000	Recovery Standard

Note: (1) Results are corrected for surrogate recovery (2) ND = not detected
(3) DL = detection limit (pg/g/analyte peak) (4) N/A = not applicable
(5) NDR = not detected due to incorrect isotopic ratio (6) NDR concentrations are included in total TEQ
(7) pg/g values in brackets are not taken into account for the totals calculations
(8) * Calculated ½ elution times using reference: Nevalainen, et al., *Environ. Sci. and Technol.*, 1994, 28, 1341-1347

Approved by:_____ Date: _____.

G. Pesticide Sample Data Sheet

Sample: Proc-blk 10/2/97
Sample Type: Procedural Blank,
Laboratory: I.O.S. Regional Contaminants Laboratory
Site: N/A,
Sampling Date: N/A
Sample Processing Date: 10-Sep-98
Sample Wt. Submitted for Analysis (gm): N/A

Sample Net Wt. Extracted (g): 0.06
GC Column & MS: DB5-60m Autospec
% Lipid: N/A
% Moisture: N/A
Initial Calibration Date: 27-Sep-98
Analysis Date: 27-Sep-98
File #s: PEST-A-3241 and PEST-B-3121*

Congener	pg/g	DL	Congener	pg/g	DL
1,3,5-Trichlorobenzene	20.75	6.70	Oxychlordane*	ND	47.03
1,2,4-Trichlorobenzene	4469.33	6.70	trans-chlordane*	39.80	32.08
1,2,3-Trichlorobenzene	294.00	6.70	o,p'-DDE	ND	102.11
			alpha-endosulfan	NDR(5361.83)	151.65
1,2,3,5-Tetrachlorobenzene/			cis-chlordane*	NDR(61.10)	58.80
1,2,4,5-Tetrachlorobenzene	58.45	4.41	trans-nonachlor*	ND	167.91
1,2,3,4-Tetrachlorobenzene	59.90	4.41	Dieldrin	ND	405.66
			p,p'-DDE	533.56	85.62
Pentachlorobenzene	274.83	4.13	o,p'-DDD	ND	34.63
			Endrin*	ND	214.75
alpha-HCH	ND	265.19	p,p'-DDD	ND	42.60
Hexachlorobenzene	826.18	9.38	cis-nonachlor*	ND	119.35
beta-HCH	ND	265.19	o,p'-DDT	ND	152.58
gamma-HCH	ND	401.23	p,p'-DDT	ND	211.65
Heptachlor	ND	101.29	Methoxychlor	ND	371.95
Aldrin	ND	141.15	Mirex	NDR(238.18)	20.86
Heptachlor epoxide*	66.84	25.74			

Surrogate	Amount Added (pg)	% Recovery
^{13}C-1,2,3-Trichlorobenzene	2972	46
^{13}C -1,2,3,4-Tetrachlorobenzene	2972	53
^{13}C -Pentachlorobenzene	2972	61
^{13}C -Hexachlorobenzene*	2972	56
^{13}C -lindane	3140	73
^{13}C -p,p'-DDE	3004	102
^{13}C -Mirex	2304	82
^{13}C -PCB 111	2017	Recovery Standard

Note:
(1) Results are corrected for surrogate recovery
(2) ND = not detected
(3) DL = detection limit (pg/g/analyte peak)
(4) N/A = not applicable
(5) NDR = not detected due to incorrect isotopic ratio
(6) Analysis done in two parts. Asterisk (*) denotes concentrations determined from the second analysis
(7) Compounds are listed according to elution order

Approved by:_____ Date:_____

APPENDIX XIII

Data Quality Assurance Guidelines

A. Basic Rules for all Data QA

- S/N: All accepted peaks, both channels, must be at least three times the height of the adjacent noise. All peaks that are smaller than this height are assigned ND/MDL.
- Isotope ratio: All accepted peaks must agree with their own specific isotope ratio range. All peaks that do not or cannot be reasonably adjusted to agree with the ratio range must be assigned as "NDR (concentration)".
- RRF: The concentration calculated is based on the best attainable peak shapes and uses the compounds' RRF (if it is a target compound) or the average homologue RRF (if it is not a target compound).
- Retention time: All target peaks must elute at the experimentally or predicted retention time for that target compound.

B. Data Quality Assurance Guidelines and Procedures

1) Peak Area: Adjustments made to peak areas must make sense with respect to the magnitude of the change. Any adjustment that results in a change in the isotope ratio must be documented on the chromatogram.
2) MDL: If the data system calculates an MDL that is greater than the minimum MDL for that type of analysis, see Appendix XIV, a manual MDL should be calculated. Minimum MDLs are based on a sample weight of 10 g. The noise section used for an MDL calculation must be distinct from major peak tails.
3) Coeluters: Peak width is the best guide to determining if there are coeluters in a symmetrical peak. This is particularly useful in cases where there are matching surrogate and native compounds. There is an approximate 2-second time difference between the retention time of a surrogate and its corresponding native. Abnormally wide peaks may indicate co-eluters and necessitate an adjustment to the total number of peaks in a homologue series, which is especially important in PCDD/F analysis.
4) Changes to surrogate internal standards: If adjustments are made to a surrogate internal standard's peak areas, concentrations of native compounds targeted against that particular surrogate must be adjusted.
5) Split samples: For samples that are split during sample preparation the following adjustments are required: samples submitted with a unit weight (i.e. filters, polyurethane foam samples (PUFs), incinerator samples), data must be reported as a total amount in the sample (units = pg or ng). When these samples are split the native concentrations are multiplied by the inverse of the split percent, after it has been targeted to reflect the total amount of analyte in the original sample. The sample weight field in the final report should read N/A.
6) Samples submitted with a sample weight (i.e. tissue, darts, sediment) are reported as a concentration (units = pg g^{-1}). Adjustments for a split must be made to the sample

weights and surrogate internal standard amounts, and if the total amount of analyte is being reported also to the native concentrations and MDL values.

7) Procedural blanks: Procedural blank weights should reflect the weights of the samples with which they are being released. The laboratory usually processes samples with the following types of weights: 10 g, 5 g, 1 g, 0.1 –0.3 g. If a blank is being used in a batch of samples of various weights, several versions of the blank are produced. Both the MDLs and analyte concentrations are affected by a weight change.
8) Non-Detect Labels: The following non-detect labels are used during QA:
   - ND/MDL not detected, lower than MDL or 3:1 S:N
   - ND/COR not detected, peaks in both mass channels > 3 seconds apart
   - ND/SH not detected, shape (adjustment would make it ND/MDL)
   - NDR not detected, isotope ratio incorrect and not adjustable
   - ND/ether not detected, ether peak area > 5% of total peak area of PCDF.
9) Lock mass: If possible, adjustments are made for any compounds affected by lock mass deviations. Lock mass interferences to target compounds are reported with a (**).

C. Procedures specific to analysis

PCDD/Fs

a. Target: All target analytes must be quantified as individual congeners using their own, specific, RRF. If a target analyte has a co-eluting peak, the total peak area attributable to the target peak is determined and the concentration for the target analyte is reported. The balance of the peak attributable to non-target analyte(s) is calculated based upon the average homologue RRF, with the appropriate number of peaks.
b. Non-targets: All non-target compounds are quantified using an average homologue RRF. If a non-target analyte has a coeluting peak, it may be counted as multiple peaks as long as they agrees with known relative retention times for non-target and the total number of peaks for a homologue series does not exceed the maximum number possible for that homologue series. All peaks (target and non-target) with isotope ratios within the correct range are included in the concentration total and peak number total of the homologue series.
c. Ethers: Individual PCDF peaks are assigned as ND/ether if the interfering ether peak area is ≥ 5% of the interfered-PCDF total peak area.
d. NDR: NDR values are calculated for target peaks only; non-target NDR peaks become ND. NDR values of target peaks are not included in concentration totals.

PCBs

a. Targets: Only target compounds are reported for PCB analysis. All non-target peaks are ignored.
b. Decomposition: Decomposition occurs from higher-chlorinated PCBs at identical retention times. An automatic correction for this contribution is made by CDAS on the lower-chlorinated PCBs. For a manual decomposition calculation, 3% of the area of the higher-chlorinated PCB is subtracted from that of the lower-chlorinated PCB.
c. PCB 127 correction: PCBs 127 and 105 coelute and also fractionate between carbon fibre fraction II (MO-PCB) and III (NO-PCB). The only problematic combination has been found to be 105 contributing 127 in fraction III. The peak areas of surrogate and

native compounds from analyses of both fractions are used to calculate a correction for PCB 127 in fraction III/IV.

DO- and MO-PCBs

a. DiCB: Results for di-CBs 7/9, 6 and 8/5 are used from the DO-PCB report UNLESS the ^{13}C PCB-28 recovery into the DO-PCB fraction is too poor (< 10%). In this case, the di-CB results are used from the MO-PCB report. The remaining di-CB (4/10) is targeted against ^{13}C PCB 52 and is always part of the DO-PCB report.
b. TriCB: The tri-CBs fractionate between the MO and DO fractions. To ensure good quantification of these compounds, the following procedure is followed:
   - Recalculation of PCBs 31 and 28: The concentrations of PCBs 31 and 28 are recalculated by using the area/height ratio from ^{13} PCB 28 in both the MO-PCB and DO-PCB fractions.
   - MO/DO split percentage: The split of 13C PCB 28 between the mo-pcb and do-pcb fractions is calculated. The tri-CB results are used from the fraction that contains >65% of the ^{13}C PCB 28. If either fraction contains ≤65% of the ^{13}C PCB 28, PCBs 26, 25, 31 and 28, then results of both fractions are averaged. Also, when averaged data is used, PCBs preceding PCB 26 are used from the DO-PCB analysis; PCBs following PCB 28 are used from the MO-PCB analysis.
   - Data source: If the tri-CBs are solely quantified from the DO-PCB fraction, the % recovery of the ^{13}C PCB 28 from the DO-PCB is transferred to that of the MO-PCB.

c. PCB 111: Due to a coeluting peak, PCB 111 must be adjusted based on a 70 second later elution time than PCB 101.
d. MO PeCBs: There are two MO ^{13}C Pe-CB surrogate internal standards. All MO Pe-CBs are targeted against ^{13}C PCB 105 except for PCB 118, which is targeted against ^{13}C PCB 118.
e. DO-PCBs: DO-PCBs not routinely observed are: 30, 69, 43, 65, 62, 98, 121, 113, 116/125/117, 133, 165, 186, 173, 204.
f. DO-PCB peak shape: Peak shapes can be slightly non-symmetrical for the following DO-PCB target coeluters: 27/24, 59/42, 71/41/64, 170/190. Any other peaks, even if they have more than one assigned target, should be symmetrical. Adjustments should definitely be made to PCBs 82 and 129 because they suffer from decomposition and/or poor shape.
g. DO-PCB MDLs: Two MDL values are calculated for each of the HxCB and OcCB homologue because the analyses are done in two functions each. The target HxCB and OcCB will be assigned the MDL of the corresponding function.

APPENDIX XIV

QA Control Information

A. Control Limits for PCDD/Fs

Surrogate internal standard surrogate recoveries must be between 30 and 130% except for TCDD. TCDD surrogate internal standard surrogate recoveries must be between 40 and 130%.

Compound	Minimum MDL	Isotope Ratio Range
TCDF	0.05	0.65-0.89
TCDD	0.06	0.65-0.89
PeCDF	0.06	1.32-1.78
PeCDD	0.08	0.53-0.71
HxCDF	0.08	1.05-1.43
HxCDD	0.10	1.05-1.43
HpCDF	0.10	0.88-1.20
HpCDD	0.12	0.88-1.20
OCDF	0.12	0.76-1.02
OCDD	0.14	0.76-1.02

B. Control Limits for PCBs

Homologue Class	Isotope Ratio Range	Midpoint
Di	1.23-1.85	1.54
Tri	0.82-1.24	1.03
Tetra	0.62-0.92	0.77
Penta	1.24-1.86	1.55
Hexa	0.99-1.49	1.24
Hepta	0.83-1.25	1.04
Octa	0.71-1.07	0.89
Nona	0.62-0.94	0.78
Deca	0.94-1.40	1.17

C. Minimum Method Detection Limits for PCBs

PCB	(pg g^{-1})
DO	0.90
MO	0.10
NO	0.04

D. Control Limits for PBDEs

Homologue Class	Isotope Ratio Range	Midpoint
MoBDE	0.82-1.22	1.02
DiBDE	0.41-0.61	0.51
TriBDE	0.82-1.22	1.02
TeBDE	0.41-1.61	0.51
TeBDE (BDE-77 only)	0.54-0.82	0.68
PeBDE	0.82-1.22	1.02
HxBDE	0.54-0.82	0.68
HpBDE	0.82-1.22	1.02
OcBDE	0.62-0.92	0.77
NoBDE	0.82-1.22	1.02
DeBDE	0.66-0.98	0.82

E. Control Limits for PCDEs

Compound	Isotope Ratio Range	Midpoint
MoCDE	2.42-3.64	3.03
DiCDE	1.23-1.85	1.54
TriCDE	0.82-1.24	1.03
TeCDE	0.62-0.94	0.78
PeCDE	0.84-1.26	1.05
HxCDE	0.62-0.94	0.78
HpCDE	1.24-1.86	1.55
OcCDE	0.99-1.49	1.24
NoCDE	0.83-1.25	1.04
DeCDE	0.71-1.07	0.89

F. Control Limits for Pesticides

Compounds Fraction 1 / Fraction 2	Isotope Ratio Range	Midpoint
1,3,5-trichlorobenzene (triCB), 1,2,4-triCB, 1,2,3-triCB	0.83-1.25	1.04
1,2,3,5-tetrachlorobenzene (teCB), 1,2,4,5-teCB, 1,2,3,4-teCB	0.62-0.94	0.78
Pentachlorobenzene	1.25-1.87	1.56
alpha-hexachlorocyclohexane (HCH), beta-HCH, gamma-HCH	1.66-2.50	2.08
Hexachlorobenzene	1.00-1.50	1.25
heptachlor	1.00-1.50	1.25
aldrin, dieldrin	1.24-1.86	1.55
o,p'-DDE, p,p'-DDE	1.25-1.87	1.56
o,p'-DDD, p,p'-DDD, o,p'-DDT, p,p'-DDT	1.25-1.87	1.56
13C-p,p'-DDT	1.33-1.79	1.56
Methoxychlor	5.33-7.99	6.66
Mirex	1.00-1.50	1.25

Fraction 3

heptachlor epoxide	1.00-1.50	1.25
Oxychlordane	0.83-1.25	1.04
trans-chlordane, cis-chlordane	0.83-1.25	1.04
trans-nonachlor, cis-nonachlor	0.71-1.07	0.89

G. Dioxin/Furan Isomers

When using this table, adjust your specific retention times relative to the 2,3,7,8-substituted compounds

TCDF, 38 ISOMERS	Elution time
1,3,6,8-w	21:58
	22:32
	22:50
	23:10
	23:36
	24:03
	24:21
	24:29
	24:48
	25:16
	25:38
2,3,7,8	25:57
	26:40
	27:01
1,2,8,9-w	28:57
TCDD, 22 ISOMERS	
1,3,6,8-w	23:35
	24:00
	24:26
	25:21
	25:48
1,4,7,8	25:56
1,2,3,4	26:52
1,2,3,7/1,2,3,8	27:05
2,3,7,8	27:14
1,2,6,7	27:52
1,2,7,8	28:19
	28:54
1,2,8,9-w	29:06
PeCDF, 28 ISOMERS	
1,3,4,6,8-w	29:38
	29:43
	31:37
	31:56
	32:15
	32:33
	32:58
	33:23
1,2,3,7,8	33:31
	34:07
2,2,4,7,8	35:00
	35:14
1,2,3,8,9-w	36:38

PeCDD, 14 ISOMERS	Elution time
1,2,4,6,8/1,2,4,7,9-w	32:20
	33:12
	33:45
	34:01
	34:17
	34:37
	34:48
	35:11
	35:20
1,2,3,7,8	35:44
	36:00
1,2,3,8,9-w	36:33
HxCDF, 16 ISOMERS	
1,2,3,4,6,8-w	38:25
	38:40
	39:10
	39:30
1,2,3,4,7,8	40:09
1,2,3,6,7,8	40:20
	41:08
2,3,4,6,7,8	41:18
1,2,3,7,8,9	42:24
1,2,3,4,8,9-w	42:34
HxCDD, 10 ISOMERS	
1,2,4,6,7,9/1,2,4,6,8,9	39:27
	40:16
	40:40
	41:07
1,2,3,4,7,8	41:35
1,2,3,6,7,8	41:44
1,2,3,4,6,7-w	42:07
1,2,3,7,8,9	42:11
HpCDF, 4 ISOMERS	
1,2,3,4,6,7,8-w	45:04
	45:25
	45:39
1,2,3,4,7,8,9-w	47:06
HpCDD, 2 ISOMERS	
1,2,3,4,6,7,9-w	45:36
1,2,3,4,6,7,8-w	46:38
OCDF	50:44
OCDD	50:39

APPENDIX XV

Examples of Quality Control Values for Certified Reference Materials

All concentrations in pg g^{-1} wet weight

TROUT CRM

Dioxin/Furan	RDL Mean Concentration	-2 STD.DEV.	+2 STD.DEV.
2,3,7,8-TCDD	17.34	15.90	18.78
1,2,3,7,8-PeCDD	3.74	3.06	4.76
1,2,3,4,7,8-HxCDD	0.4	0.16	0.64
1,2,3,6,7,8-HxCDD	2.55	2.09	3.01
1,2,3,7,8,9-HxCDD	0.5	0.14	0.86
1,2,3,4,6,7,8-HpCDD	0.63	-0.05	1.31
1,2,3,4,6,7,8,9-OCDD	2.02	-0.06	4.1
2,3,7,8-TCDF	23.91	18.25	29.57
1,2,3,7,8-PeCDF	4.91	3.85	5.97
2,3,4,7,8-PeCDF	14.74	10.54	17.54
1,2,3,4,7,8-HxCDF	6.33	5.53	7.13
1,2,3,6,7,8-HxCDF	1.76	1.28	2.24
2,3,4,6,7,8-HxCDF	1.08	0.42	1.42
1,2,3,7,8,9-HxCDF	0.18	-0.18	0.54
1,2,3,4,6,7,8-HpCDF	0.53	0.31	0.75
1,2,3,4,7,8,9-HpCDF	0.15	-0.05	0.35
1,2,3,4,6,7,8,9-OCDF	0.39	-1.1	1.41

TROUT CRM

Coplanar PCB	RDL Mean Concentration	-2 STD.DEV.	+2 STD.DEV.
PCB 15	10	2	18
PCB 11	16	8	24
PCB 13	4	-1	9
PCB 37	107	30	185
PCB 35	21	-31	73
PCB 36	1	-1	3
PCB 39	9	5	14
PCB 80	288	-45	622
PCB 79	38	2	74
PCB 78	2	-2	5
PCB 81	175	154	196
PCB 77	2279	1840	2717
PCB 127	807	-218	1833
PCB 126	802	679	924
PCB 169	69	55	82

F2

TROUT CRM

Mono-ortho PCB	RDL Mean Concentration	-2 STD.DEV.	+2 STD.DEV.
PCB 60	13382	6571	20193
PCB 72	232	-3	468
PCB 68	187	32	342
PCB 58	463	-263	1189
PCB 61	16360	6904	25816
PCB 70	28567	9276	47858
PCB 66	50621	25291	75951
PCB 55	88	35	142
PCB 123	4939	322	9556
PCB 118	136154	115401	156907
PCB 114	3869	2372	5365
PCB 105	66445	55286	77603
PCB 111	214	-287	714
PCB 124	4606	2866	6345
PCB 108	11762	5356	18168
PCB 122	884	368	1399
PCB 159	141	92	190
PCB 167	8438	5552	11325
PCB 156	14553	10035	19070
PCB 157	4042	2708	5376
PCB 162	1576	993	2158
PCB 189	1177	469	1884

HERRING CRM

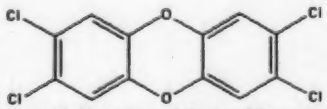
Di/tri/tetra-ortho PCB	RDL Mean Concentration	-2 STD. DEV.	+ 2 STD. DEV.
PCB 4/10	10.4	4.4	16.3
PCB 19	3.1	1.3	4.9
PCB 18	72.9	50.6	95.3
PCB 17	15.4	8.5	22.4
PCB 27/24	12.4	8.9	15.9
PCB 16/32	51.8	29.6	73.9
PCB 50	0.2	0.1	0.3
PCB 53	22.8	10.0	35.6
PCB 51	4.9	2.4	7.4
PCB 45	10.0	7.5	12.4
PCB 46	4.2	3.1	5.3
PCB 73/52	655.0	554.3	755.6
PCB 49	201.7	162.0	241.4
PCB 47/75/48	157.3	132.1	182.6
PCB 44	305.6	252.3	359.0
PCB 59/42	120.8	100.3	141.3
PCB 71/41/64	402.0	323.4	480.7
PCB 40	33.2	26.1	40.3
PCB 96	0.6	-0.1	1.3
PCB 103	4.5	2.7	6 2
PCB 100	4.4	2.8	6.1
PCB 94	1.8	1.2	2.4
PCB 102/93	13.8	7.6	19.9
PCB 95	627.3	493.4	761.1
PCB 88	4.2	0.8	7.6
PCB 91	94.9	74.6	115.2
PCB 92/84	207.6	165.1	250.0

PCB 89	79.1	60.1	98.2
PCB 101/90	1240.8	1004.2	1477.4
PCB 99	624.7	504.7	744.8
PCB 119	46.6	37.5	55.7
PCB 109/83	34.0	26.5	41.5
PCB 97/86	176.5	138.1	214.8
PCB 115/87	372.4	303.1	441.7
PCB 85	200.3	160.8	239.7
PCB 110	814.1	617.8	1010.4
PCB 82	63.1	47.0	79.2
PCB 155	1.1	0.5	1.6
PCB 150	2.2	1.0	3.3
PCB 152	0.2	0.2	0.3
PCB 148	2.6	1.2	4.0
PCB 136	87.2	49.8	124.7
PCB 154	21.4	11.1	31.8
PCB 151	277.0	172.8	381.1
PCB 135/144	164.1	98.1	230.1
PCB 147	19.9	11.4	28.4
PCB 149	900.0	568.8	1231.1
PCB 139/140	6.5	3.0	10.1
PCB 143/134	27.2	14.2	40.3
PCB 142/131	6.0	-8.1	20.0
PCB 146/161	291.1	207.7	374.4
PCB 132/153	1832.2	1496.0	2168.4
PCB 168	224.5	143.3	305.7
PCB 141	159.0	134.7	183.3
PCB 137	46.0	37.0	55.0
PCB 130	153.2	132.6	173.9
PCB 160/163/164/138	1477.6	1250.4	1704.8
PCB 158	76.9	54.4	99.5
PCB 129	20.6	16.4	24.8
PCB 166	4.5	3.4	5.7
PCB 128	175.7	146.2	205.2
PCB 188	1.4	0.6	2.1
PCB 184	0.9	0.4	1.5
PCB 179	77.9	48.2	107.7
PCB 176	30.5	20.8	40.3
PCB 178	62.2	37.3	87.0
PCB 175	9.6	5.2	14.0
PCB 187/182	435.6	333.0	538.2
PCB 183	116.9	69.5	164.3
PCB 185	15.6	10.0	21.3
PCB 174/181	148.1	101.6	194.6
PCB 177	127.2	92.8	161.6
PCB 171	47.4	36.1	58.6
PCB 173	1.1	0.3	1.9
PCB 192/172	36.6	30.7	42.4
PCB 180	379.6	316.9	442.3
PCB 193	25.4	19.7	31.2
PCB 191	5.7	4.2	7.2
PCB 170/190	158.6	124.8	192.3
PCB 202	29.8	13.2	46.4
PCB 200	24.6	11.9	37.4
PCB 197	4.8	3.2	6.3
PCB 199	7.0	5.3	8.7
PCB 198	2.8	1.6	4.0
PCB 201	75.4	39.3	111.4

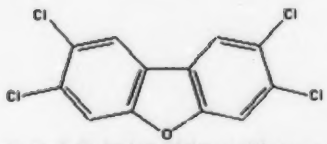
PCB 203/196	77.6	54.9	100.3
PCB 195	16.7	12.9	20.5
PCB 194	53.7	43.7	63.7
PCB 205	2.1	1.4	2.8
PCB 208	10.9	8.8	13.0
PCB 207	6.4	5.2	7.6
PCB 206	25.9	11.7	40.2
PCB 209	17.6	12.9	22.3

APPENDIX XVI

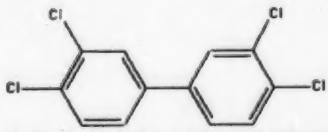
Examples of chemical structures



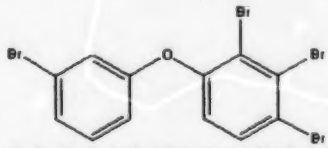
2,3,7,8-tetrachlorodibenzo-*p*-dioxin
(2,3,7,8-TCDD)



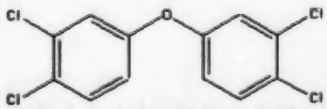
2,3,7,8-tetrachlorodibenzo-*p*-furan
(2,3,7,8-TCDF)



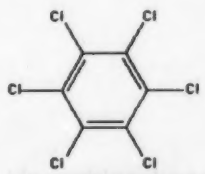
3,3',4,4'-tetrachlorobiphenyl
(PCB 77)



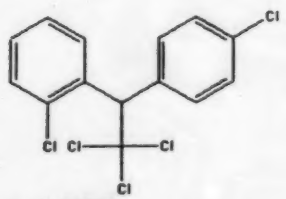
2,3,3',4-tetrabromodiphenyl ether
(BDE-55)



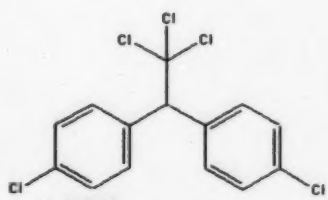
3,3',4,4'-tetrachlorodiphenyl ether
(CDE-77)



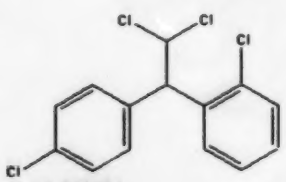
Hexachlorobenzene (HCB)



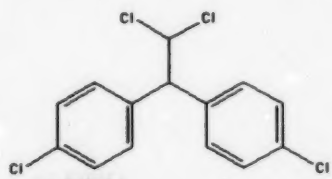
o,p'-DDT
(o,p'-dichlorodiphenyltrichloroethane)



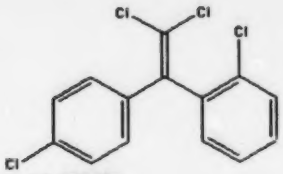
p,p'-DDT
(p,p'-dichlorodiphenyltrichloroethane)



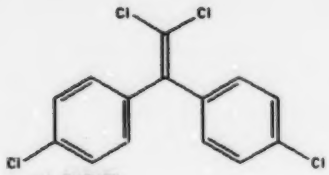
o,p'-DDD
(o,p'-dichlorodiphenyldichloroethane)



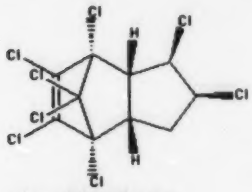
p,p'-DDD
(p,p'-dichlorodiphenyldichloroethane)



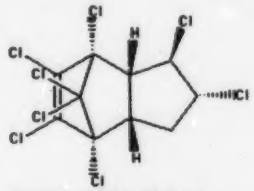
o,p'-DDE
(o,p'-dichlorodiphenyldichloroethylene)



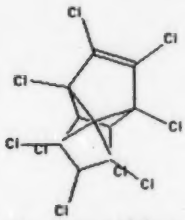
p,p'-DDE
(p,p'-dichlorodiphenyldichloroethylene)



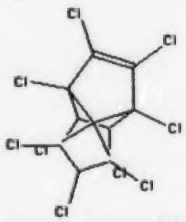
cis-chlordane



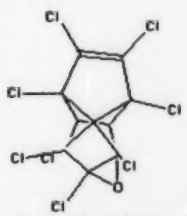
trans-chlordane



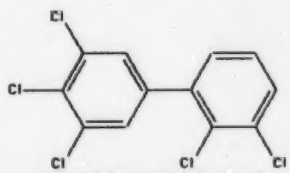
cis-nonachlor



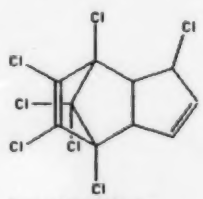
trans-nonachlor



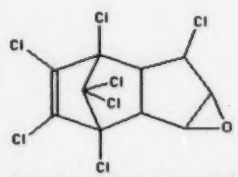
oxychlordane



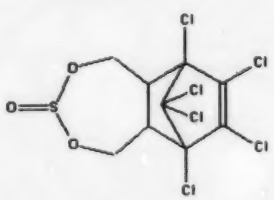
pentachlorobiphenyl



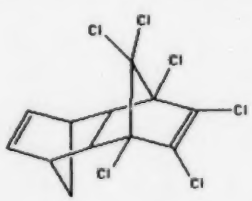
heptachlor



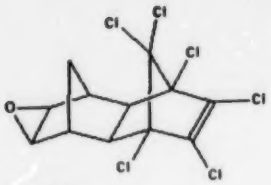
heptachlor epoxide



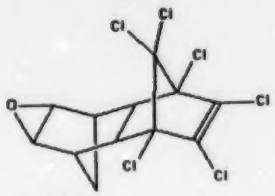
alpha-endosulfan



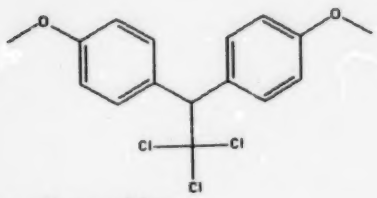
Aldrin



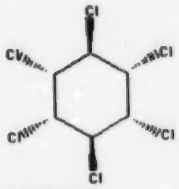
endrin



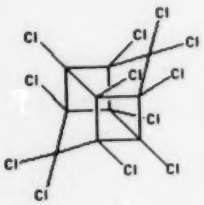
dieldrin



methoxychlor



lindane
(gamma-hexachlorocyclohexane)



Mirex

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